

# Preparation of poly(ethylene-*co*-dicyclopentadiene) copolymers and a study on their post-polymerization epoxidation

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**Abstract** The copolymerization of ethylene with dicyclopentadiene (DCP) using the metallocene catalyst *rac*-dimethylsilylbis(indenyl)zirconium dichloride ( $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ ) proceeds with high activity producing materials with DCP incorporations of 0.5–2.7 mol%. The residual olefin moiety of the DCP comonomer is still available for reaction following polymerization and was epoxidized using  $\text{H}_2\text{O}_2$  and formic acid. This reaction was optimized and proceeds with good conversion and the resulting materials show increased physical properties compared to the untreated copolymers.

**Keywords** Polyethylene-*co*-dicyclopentadiene · Metallocene catalysts · Epoxidation · Polymers

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## Introduction

The ability to instill functionality into polyolefins is one of the long sought after capabilities in polyolefin chemistry. The introduction of high concentrations of polar monomers via high pressure polymerizations with comonomers such as acrylate and vinyl acetate has been a successful commercial process for many years [1, 2]. These types of high pressure processes produce materials which are not as well defined as materials produced via low pressure; coordination–insertion processes [3–5]. In coordination–insertion processes the activity of the transition metal catalyst is limited due to the oxophilic nature of the comonomers. Late transition metal catalysts, which have lower sensitivity to polar monomers, can be used in the process; however, the incorporation of the polar monomer remains low in comparison to monomers such as  $\alpha$ -olefins and cyclic monomers. A strategy which has had some success is the copolymerization of olefins with comonomers which can be subsequently modified via post-polymerization modification either through solution chemistry or reactive extrusion.

The nature of the comonomers which can be used for these types of materials is limited by the interaction of the monomer with the catalyst to be used. The chemistry to modify the structure of a number of pendant polymer functionalities is known [6, 7] and the modification of pendant dienes is well established [8, 9]. These comonomers offer the advantage that the reactive groups (olefins) do not have unfavorable interactions with the catalytic metal centers. The use of symmetric dienes (in which both olefin segments possess the same reactivity to the metal center) in copolymerizations tend to produce crosslinked materials, and in some instances can result in the reduction of activity or even termination of the polymerization due to back-biting and secondary insertions. Therefore, asymmetric dienes, and in particular those that have an olefin which is much less available to the catalyst metal center are desirable. Two strategies are commonly pursued, the use of dienes with  $\alpha$  and internal olefins, and the use of cyclic dienes.

The copolymerization of ethylene with dicyclopentadiene (DCP) has previously been reported in this and other laboratories [10–12]. It was noted that the materials produced had a tendency to crosslink over time, which resulted in materials which were difficult to process; however, it indicated that the residual olefinic moiety in the comonomers was still available for reaction, and as such suggested that the material was suitable for post-polymerization functionalization. The post-polymerization functionalization of these types of materials has been reported in the literature using organic peroxides [13]. It has been reported in the patent literature that the use of hydrogen peroxide can epoxidize residual pendant olefinic moieties by itself [14], or in the presence of a carboxylic acid [15, 16]. In this contribution, the effect of post-polymerization processing on the crosslinking behavior of the poly(ethylene-*co*-DCP) and the post-polymerization epoxidation of the materials using hydrogen peroxide and formic acid are discussed.

## Materials and procedures

### Materials

The metallocene catalyst, *rac*-dimethylsilylbis(indenyl)zirconium dichloride ( $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ ), was obtained from Boulder Scientific Company and used without further purification. Methylaluminoxane (MAO) was purchased from Huntsman (10.7 wt% in toluene) and used as received. Toluene was purified by distillation over sodium metal and benzophenone and dispensed under nitrogen. DCP (99 %) was purchased from Aldrich, distilled using a fractionating column, and stored under nitrogen. Polymerization grade ethylene (99.9 %) was obtained from AGA S.A and purified by passage through columns of BASF R3-11G and BASF R3-12 catalysts and 4 Å molecular sieves. Formic acid (85 wt%), xylenes, and hydrogen peroxide (30 vol %) were purchased from Equilab S.A. and used as received.

### Homo- and copolymerization of ethylene

Homo- and copolymerizations of ethylene were carried out in a 0.6 L Parr glass reactor, equipped with a mechanical impeller stirrer, temperature control maintained at 40–60 °C, a constant volume of 300 mL, and 2 bar of ethylene pressure. Toluene was added to the reactor and purged with nitrogen for 30 min while the system heated to the desired temperature. MAO was then injected and the solution was allowed to stir. Prior to its use in copolymerizations, the DCP was melted in a hot water bath, and the desired quantity injected under nitrogen and allowed to stir with the MAO/toluene solution. The reactor was then filled with ethylene at 2 bar, and purged through pressure swings three times. Finally, a solution of the catalyst was injected into the reactor and the ethylene pressure increased to 2 bar. The [Al]/[Zr] molar ratio was 2,000 in each of the reactions. After 30 min, the polymerization was terminated by injecting 10 mL of a 10 vol% solution of hydrochloric acid in methanol. The product was filtered and the polymer washed successively with distilled water, ethanol, and acetone, then dried completely under vacuum at room temperature. The reactions were repeated at least once and the average values of activity are reported.

### Epoxidation of the polymeric materials

A given amount of the dry polymer (2–5 g) and a Teflon stir bar were added to a round-bottom flask, 0.5 or 1.0 L depending on batch size, and the flask half filled with xylenes and heated in an oil bath. Once the polymer had begun to dissolve, as indicated by a color change from bright white to translucent, formic acid and the hydrogen peroxide were added. A water-jacketed condensing column was attached to the round-bottom flask and the reaction heated at reflux for 1 h. The flask was removed from the oil bath and the contents transferred to a large 1–2 L beaker. Ethanol (96 %, Equilab) was added to the beaker to precipitate the polymer. The solution was allowed to cool and then filtered. The polymeric material was then

dissolved in hot xylenes and reprecipitated via the addition of ethanol to remove any residual formic acid. A modified procedure, which was found to increase the conversion of the olefinic moiety in the polymer, involved the addition of a second aliquot of hydrogen peroxide once the solution reached reflux.

### Characterization of the copolymers

Polymer samples were analyzed using differential scanning calorimetry (DSC) measurements on a TA Instruments Modulated DSC 2920. The samples were exposed to two thermal cycles, from 20 to 180 °C, at a heating rate of 10 °C/min, the values reported are from the second cycle in order to eliminate any thermal history. Polymer crystallinity was calculated by dividing the crystallization enthalpy obtained in the second thermal cycle by the theoretical value for 100 % crystalline polyethylene (290 J/g) [17].

The molecular weight of the polymers was determined by gel permeation chromatography (GPC) using a Waters Alliance model 2000 GPC. The samples were first dissolved in trichlorobenzene (1 mg/mL) then filtered prior to their analysis. Polystyrene standards were used for calibration of the columns.

The comonomer content in the copolymers was determined by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR in a Varian Innova 300 spectrometer operating at a Larmor frequency of 75 MHz and the peak assignments based on those reported in the literature [11].

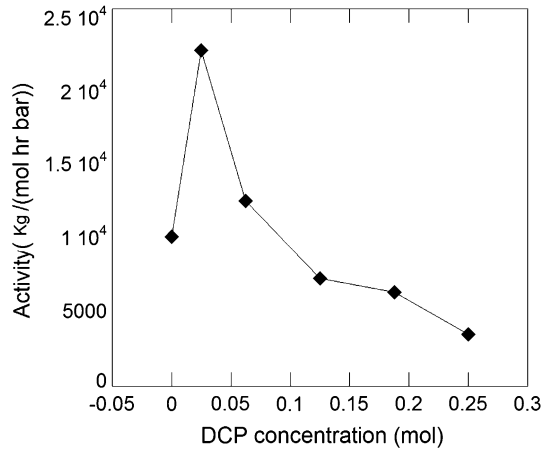
The conversion of the residual olefinic moiety of the copolymers post-modification was confirmed via FTIR, through the appearance of the signal at  $835\text{ cm}^{-1}$ , which has been attributed to the formation of an oxirane [13].

The mechanical properties were measured using a HP D500 dynamometer. The samples were melt pressed at 165 °C and 50 bars pressure using a hydraulic press to a thickness of ca 0.2 mm microns and cooled under pressure. Samples for analysis were then cut using a stainless steel die to the dimensions and shape specified in ASTM D638 M-I. The dynamometer was run at a rate of 50 mm/min at 25 °C and 35 % RH. A minimum of three samples were tested for each material and the average values are reported.

## Results and discussion

### Homo- and copolymerization catalytic behavior

The copolymerization of ethylene with DCP has been the focus of numerous studies and reviews and has been previously discussed by this group. The inexpensive nature of DCP in comparison to other comonomers and the presence of a sterically unavailable secondary olefin in its structure make it a material of great interest. In this study, it was found that the activities of the polymerizations were very sensitive to the concentration of DCP used in the reaction as shown in Fig. 1 and listed in Table 1. The addition of a low concentration of DCP (0.025 mol/L) to the polymerization reaction resulted in a large increase in the activity of the system

**Fig. 1** Polymerization activity as a function of DCP concentration**Table 1** Polymerization conditions, thermal properties, and comonomer content of the copolymers

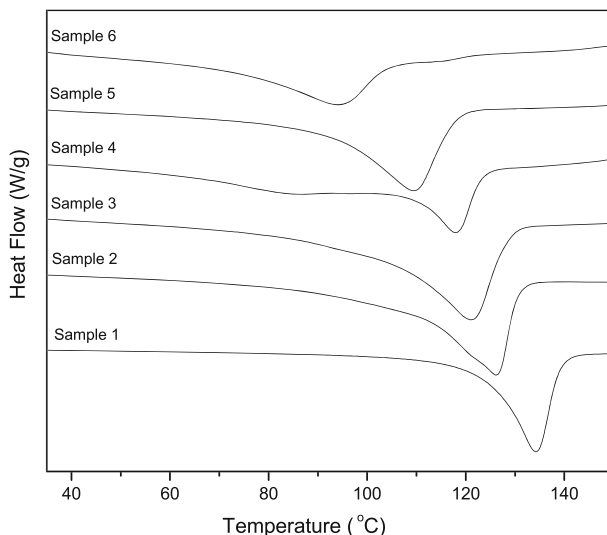
Sample	Reactor comonomer content (mol)	Melting point (°C)	Comonomer content in polymer (mol%) <sup>a</sup>	Activity <sup>b</sup>	<i>M<sub>w</sub></i> (g/mol)
1	0.0	135	0.0	9,360	381,000
2	0.025	128	0.5	22,150	336,000
3	0.0625	121	0.8	11,800	273,000
4	0.125	118	1.1	6,540	220,000
5	0.1875	108	2.5	5,562	157,500
6	0.25	94	2.7	2,700	123,000

Polymerization conditions: 2 bar ethylene, 50 °C, [Zr] =  $2.1 \times 10^{-6}$ , [MAO]/[Zr] = 2000

<sup>a</sup> Incorporation calculated by <sup>13</sup>C NMR

<sup>b</sup> Activity given in units of kg polymer mol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>

from 9,360 to 22,000 kg mol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>. The addition of higher concentrations of comonomer (0.0625 mol/L) to the reaction results in a decrease to this activity to 11,800 kg mol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>, and such decreases continue with increasing DCP content. The initial increase in activity can be attributed to the comonomer effect, which is typically observed in copolymerizations with comonomers in solution [18]. The comonomer effect is attributed to the higher concentration of comonomer present in solution when liquid monomers are used. The molecular weight of the materials decreased with increasing reactor comonomer content as shown in Table 1. At a comonomer concentration of 0.025 mol/L, the molecular weight decreased to 336,000 g/mol, a 12 % decrease compared to the homopolymerization which produced materials with molecular weights of 381,000 g/mol. Increasing the comonomer concentration to 0.0625, 0.125, 0.1875, and 0.25 mol/L decreases the molecular weight to 273000, 220000, 157500, and 123000 g/mol, respectively.



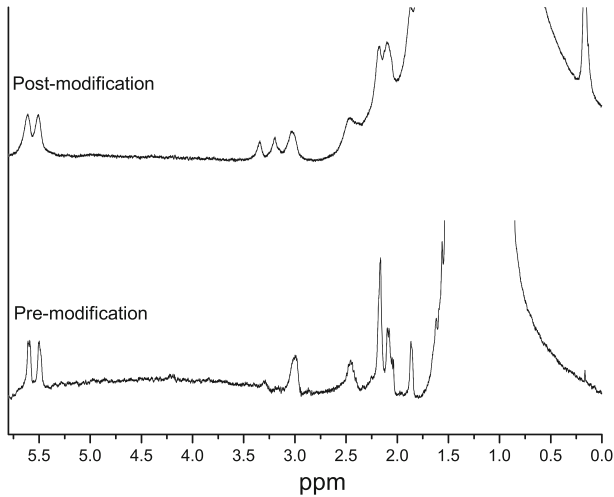
**Fig. 2** DSCs of the copolymers

### Thermal properties of the materials

The thermal properties of the materials produced are shown in Table 1 and Fig. 2. The melting point of the materials decreases steadily with the use of higher concentrations of DCP, consistent with the incorporation of comonomer into the polyethylene backbone. At low concentrations of DCP in the reactor (0.025 mol/L), the materials show a decrease in melting temperature from 135 to 128 °C, increasing the reactor concentration of DCP to 0.0625 mol/L further depresses the melting point to 121 °C. This trend continues with the melting temperature of the polymer produced using the highest reactor concentration of 0.25 mol/L having a melting temperature of 94 °C. While decreases in the molecular weight of the materials may have an effect on the melting temperature, all of the materials are of high-molecular weight and therefore should not have their melting temperature significantly reduced. The reduction in melting temperature is due to the effect of the sterically demanding DCP group which interferes with the normal packing and organization of the polyethylene crystal [19].

### NMR characterization of the polymers

The DCP content of the copolymers was analyzed by  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR ( $^1\text{H}$  NMR sample 4 is shown pre- and post-modification in Fig. 3) It was found that the content of the polymers was proportional to the DCP used in the polymerization. When 0.025 mol of DCP was used, an incorporation of 0.5 mol% was obtained increasing the reactor loading to 0.0625 mol resulted in an increase to 0.8 mol%. Further increases resulted in increasing comonomer content until a maximum was



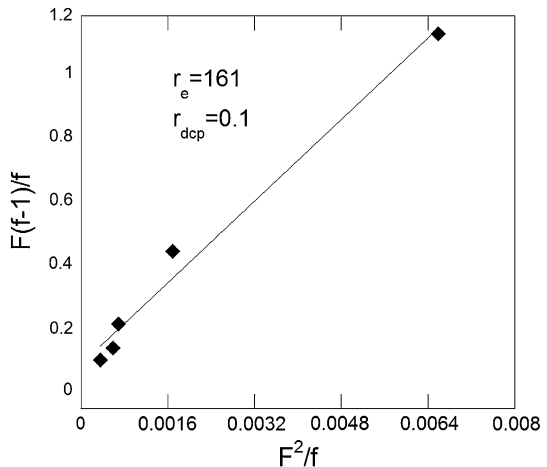
**Fig. 3** <sup>1</sup>H NMR of sample 4

reached at 2.7 mol%. While this incorporation is relatively low as a function of mol%, it actually represents a ca. 10 wt% incorporation of DCP into the polymer chain.

Reactivity ratios of ethylene and DCP

The molecular weight reduction in the copolymers with increasing comonomer concentration indicated that the DCP was having a negative effect on the molecular weight of the polymer. As such, an analysis of the reactivity ratios of the monomers using the Fineman–Ross equation was undertaken [20], the equations used are detailed below and the results are shown in Fig. 4.

**Fig. 4** Fineman–Ross plot for ethylene–DCP copolymerizations



$$\frac{F(f-1)}{f} = \left(\frac{F^2}{f}\right)r_e - r_{\text{dcp}} \quad (1)$$

where  $F$  and  $f$  are given as

$$F = \frac{\text{Concentration of ethylene in toluene}}{\text{Concentration of DCP in toluene}} \quad (2)$$

$$f = \frac{\text{moles ethylene in copolymer}}{\text{moles DCP in copolymer}} \quad (3)$$

and  $r_e$  and  $r_{\text{dcp}}$  are defined as

$$r_e = \frac{k_{ee}}{k_{e(\text{DCP})}} \quad (4)$$

$$r_{\text{DCP}} = \frac{k_{(\text{DCP})(\text{DCP})}}{k_{(\text{DCP})e}} \quad (5)$$

The  $r_e$  of 161 indicates that the insertion of DCP is very slow in comparison to that of ethylene, consistent with its large steric demands and reaction using an internal olefin. The  $r_{\text{DCP}}$  of 0.1 indicates that the rate of insertion of consecutive DCP groups into the growing chain is ten times slower than the insertion of ethylene into the DCP–metal bond. Again this is consistent with the steric bulk of the DCP monomer which all but eliminates the possibility of consecutive DCP–DCP insertions [21].

#### Crosslinking in the as-polymerized materials

It has previously been reported that polyethylene-*co*-DCP copolymers can crosslink over time, resulting in the formation of amorphous materials which are difficult to process. In this lab, it was found that the materials in these polymerizations readily crosslink. As a result of this crosslinking, the polymers would lose their melting peak in the DSC. It was suggested that this was due to the post-polymerization processing and in particular the process used to remove the residual DCP from the polymers. Previously, the polymers were heated at 60 °C for several days to drive off the residual solvent after filtration; they were then precipitated from xylenes three times to eliminate the catalyst residue and residual DCP. This process involves very high temperatures and it was thought that this could be the origin of the crosslinking. Therefore, in this study, the polymers were processed at low temperatures and kept under nitrogen to reduce the risk of crosslinking. The polymers were filtered, rinsed with acetone, and then placed into a 500 mL ball flask wrapped in aluminum foil, and dried under vacuum ( $10^{-3}$  torr) until a constant weight was achieved. It was found that when higher concentrations of DCP were used, it was necessary to heat the sample in a water bath at ca. 35 °C under dynamic vacuum in order to eliminate all DCP residues. Treatment of the polymers in this way appears to have eliminated the crosslinking phenomenon as the samples do not show changes in their DSC even after 9 months. Samples prepared using 0.125 mL of DCP maintained their melting point of 118 °C even after 9 months of storage, whereas samples heated during the filtration and drying process lost their melting point after just a few months. Therefore, the



previously observed crosslinking in the copolymers can be attributed to the conditions used during post-polymerization processing.

### Post-polymerization modification of the polymers

In order to optimize the post-polymerization process, a series of reactions were initially carried out using a sample with 1 mol% DCP incorporation, the conditions, and concentrations used in the modification are shown Table 2. The use of 25 equivalents of formic acid and hydrogen peroxide in the modification resulted in only partial conversion; the FTIR of the resulting material is shown in Fig. 5, sample A. A signal associated with the formation of an oxirane,  $835\text{ cm}^{-1}$  can be observed; the signal, however, is relatively weak and NMR analysis of the polymer reveals that only 7 % of the olefin was converted in the process indicating that the conversion was not complete. Increasing the concentration of reactants to 25:50 and 50:50,  $\text{H}_2\text{O}_2$ :FA, samples B and C; increases the conversion to higher levels as shown by FTIR. NMR analysis shows that the residual olefin present in the polymer decreased by 25 and 48 %, respectively, in these cases, indicating that while the increased concentrations resulted in higher conversion of the olefin moiety, the efficiency was relatively low. It was suspected that this was due to the conditions required, the copolymers were heated at reflux in xylenes, and therefore a substantial portion of the hydrogen peroxide and the in situ formed performic acid became inactive over the course of the reaction. It was thought that the conversion would be improved by modifying the procedure through the addition of the hydrogen peroxide in two aliquots (25 equivalents each), one in the initial stages of the reaction, the other once the reaction had reached reflux. This resulted in the epoxidation of approximately 90 % of the residual olefin moieties in the copolymer.

As this was the highest conversion obtained, the materials used for mechanical properties testing were submitted to the same procedure using the same concentration.

### Physical properties of the materials

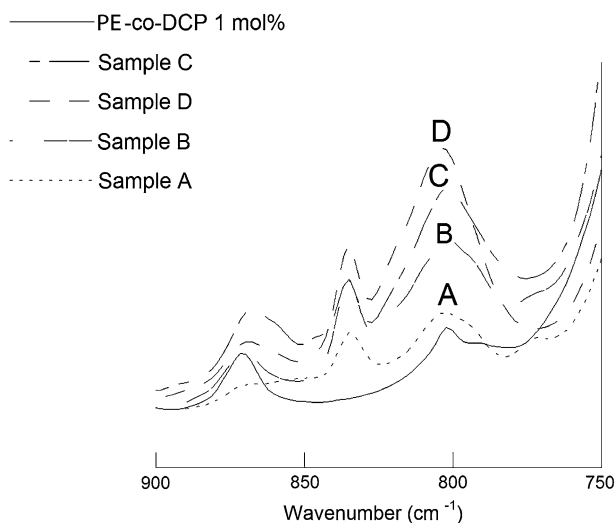
The material properties of the polymers, before and after modification are shown in Table 3 and the DSC of sample 4 pre- and post-modification in Fig. 6. It was

**Table 2** Effect of modifying post-polymerization reaction conditions on conversion results

Sample	Reactants equivalents		Melting point (°C)	Conversion (NMR) (%)
	FA	$\text{H}_2\text{O}_2$		
A	25	25	126.13	7
B	50	25	126.24	25
C	25	50	124.73	48
D	50	50 <sup>a</sup>	122.58	92

FA formic acid

<sup>a</sup>  $\text{H}_2\text{O}_2$  added in two aliquots; once the polymer was dissolved and when the system reached reflux



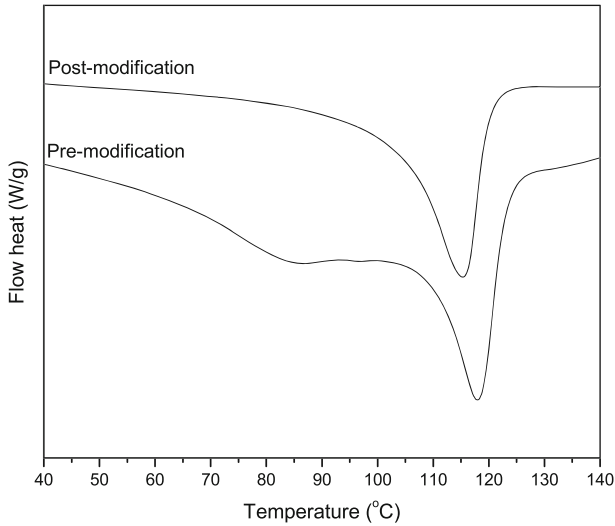
**Fig. 5** FTIR of polymer samples before and after modification, peak at  $835\text{ cm}^{-1}$  is associated with formation of an oxirane

observed that the incorporation of DCP comonomer in all cases resulted in a decrease in the Young's modulus and elongation at break. After the modification, the polymers showed a decrease in the Young's modulus in comparison to the unmodified polymers, in addition and perhaps most interestingly the modified polymers show an increase in their strain at break. This increase appeared to scale with the concentration of comonomer in the material. Polymers with relatively low concentrations, ca. 0.5 mol% showed an increase of 60 % in the elongation at break, whereas the elongation at break of the materials with 1.2 mol% comonomers nearly doubled upon epoxidation. The stress–strain curves of the materials show distinct forms, the homopolymer curve has a shape which is typical of polyolefin materials and shows a well-defined plastic region followed by the rupture of the polymer. The copolymer materials show only an elastic region in the stress–strain curve, which is

**Table 3** Thermal and physical properties of the polymers pre- and post-polymerization modification

Sample	Mp (°C)		Physical properties				Incorporation (mol%)	
	As made	After modification	As made		After modification		<sup>1</sup> H NMR	<sup>13</sup> C NMR
			YM	Strain at break	YM	Strain at break		
Homopolymer	135	–	570	220	–	–	–	–
2	128	126	216	160	170	262	0.5	0.5
4	118	115	296	225	236	303	1.0	0.8
5	108	109	91	133	77	253	1.4	1.2

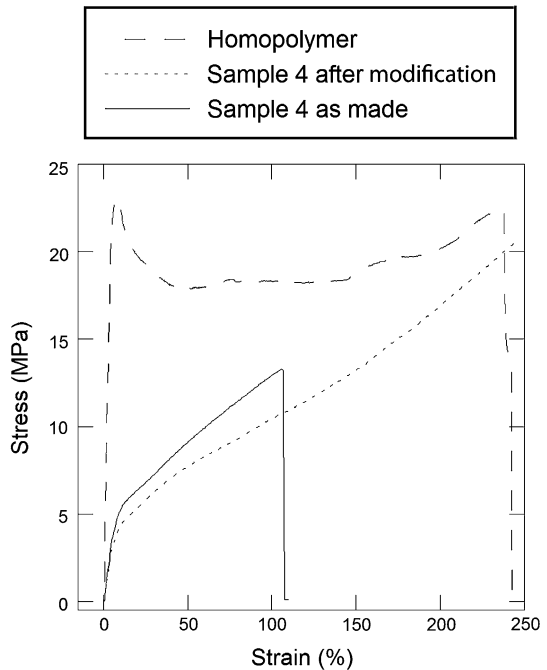
YM Young's modulus



**Fig. 6** DSC of sample 4 pre- and post-modification

associated with elastomeric materials [22]. The difference in the copolymers pre- and post-modification is clear in Fig. 7, with the post-modification materials yielding at a much larger strain than the pre-modification materials. The increase in strain at break could be due to crosslinking during the preparation (melt pressing) of

**Fig. 7** Stress–strain curves of sample 4 before and after modification. The copolymers show only an elastic region without the plastic region plateau observed in the homopolymer sample



the materials for mechanical testing. Molecular weight analysis by GPC was attempted, however, the materials are substantially less soluble, making their analysis impossible, and suggesting that they may in fact be crosslinked.

## Conclusions

The copolymerization of ethylene with DCP provides facile access to materials which can be post-polymerization modified for the production of polyethylenes which bear polar functionality. A series of such copolymers was produced over a range of comonomer content with care taken to avoid crosslinking in the processing of the materials. The modification of the residual olefin was accomplished using epoxidation chemistry, which converts the second olefin present (the cyclopentene group) in the DCP to an oxirane, and was accomplished using hydrogen peroxide and formic acid as the epoxidizing agents. The extent of the modification was found to be dependent on the concentration of the reactants used, and excess of formic acid and in particular hydrogen peroxide were necessary to achieve the maximum modification. There was a trade off in the physical properties of the materials post-epoxidation with the strain at break increasing and the Young's modulus decreasing. In addition, the materials did not exhibit a plastic region in the stress–strain curve and only exhibited an elastic behavior until the yield. The previously reported crosslinking of the unmodified copolymers was found to be a product of processing conditions and the selection of milder conditions to remove the residual DCP was found to reduce and possibly eliminate the crosslinking of the materials.

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