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Thermal crosslinking of ethene copolymers containing 1,2-cyclopropane units

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Abstract

The possibility to obtain crosslinked polyethene (XLPE) from new ethene copolymers containing cyclopropane rings (C3), synthesized by ethene/1,3-butadiene copolymerizations with a hindered metallocene catalyst, has been explored. In particular, the thermal crosslinking of these copolymers, for C3 molar content in the range 0.3–2.7%, has been studied for annealing temperatures up to 200 °C and compared with the thermal behavior of other ethene–butadiene copolymers. Only for the ethene–C3 copolymers, the annealing procedures in the temperature range 160–200 °C lead to high gel fractions. These crosslinking processes occur in reasonable times and leave nearly unaltered the polymer crystallinity. Moreover, annealing procedures up to 140 °C do not produce appreciable crosslinking. All these features suggest that these new copolymers could be suitable for possible industrial fabrication processes of XLPE.

Keywords: Ethene copolymers; Cyclopropane rings; Crosslinked polyethene

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1. Introduction

The highly strained three-member carbocycle is common in nature and sometimes occurs in multiply cyclopropanated compounds [1]. Linear as well as more complex multiply cyclopropanated architectures have been also obtained by several synthetic routes [1]. In particular, transition-metal catalysts have provided relevant opportunities for selective cyclopropanation reactions, generally involving cycloaddition between a double bond and a metal carbene [2–3].

In a recent work of some of us, an unprecedented cyclopropanation reaction through cyclopolymerization has allowed to produce methylene-1,2-cyclopropane units by copolymerization of butadiene with ethene [4–6], catalyzed by the highly sterically hindered metallocene *rac*-[CH_2(3-*tert*-butyl-1-indenyl)$_2$]$ZrCl_2$, discovered by Resconi and coworkers [7–8].

In particular, it has been found that in suitable copolymerization conditions all butadiene molecules can be inserted as cyclic monomeric units, i.e. methylene-1,2-cyclopropane units (model A in Scheme 1) together with methylene-1,2-cyclopentane units (model B in Scheme 1), in a ratio generally not far from 2:1 and both with high trans selectivity [4–6].

These new ethene copolymers containing a controlled number of reactive cyclopropane rings (thereafter cited as E–C3 copolymers) could be in principle industrially relevant since obtained with high yields from basic monomers.

In this paper it is shown that it is possible to produce crosslinked polyethene (XLPE) from E–C3 copolymers, by simple thermal treatments. In this respect, it is worth recalling that both high-density and low-density XLPE have become commonly used industrial polymers. In fact, the crosslinking of polyethene molecules into three-dimensional networks leads to significant improvements of impact strength, thermal performance, chemical resistance, wear and creep behavior and aging characteristics [9–11]. Currently, different techniques are in use for production of crosslinked polyethene; the most common technique is the radical crosslinking [11–15], initiated by peroxide or via β, γ or electron beam irradiation [16–19]. Different techniques

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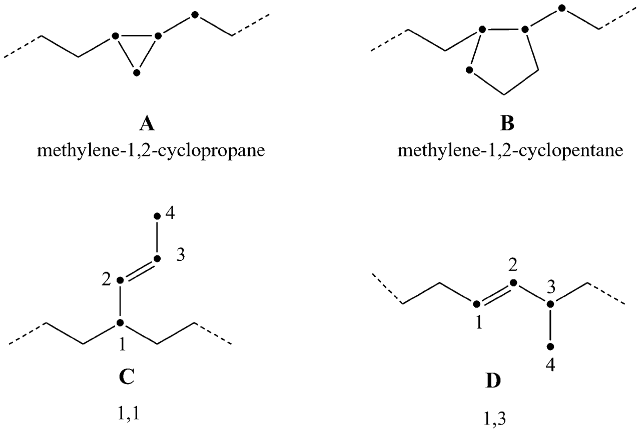

Scheme 1. Constitutional units from 1,3-butadiene in copolymers with ethene.

comprise vinylsilane grafting to the polymer chains, after initiation with a small amount added peroxide, followed by long term (hours) crosslinking at 80–90 °C at 100% relative humidity or in water [20–21].

The thermal crosslinking of E–C3 copolymers, for C3 molar content in the range 0.3–2.7%, has been explored for temperatures up to 200 °C and compared with the thermal behavior of other ethene–butadiene copolymers. This comparison has involved new ethene copolymers inserting butadiene prevailingly as 1,1 units (model C of Scheme 1, i.e. leading to double bonds as side groups) and 1,3 units (model D of Scheme 1, i.e. leading to double bonds in the main chain) [5] or only as methylene-1,2-cyclopentane units (model B in Scheme 1) [6], both recently obtained in our research group [22].

2. Experimental section

2.1. Polymerization procedure

All the operations were performed under nitrogen atmosphere by using conventional Schlenk-line techniques. Toluene was refluxed over sodium diphenylketyl for 48 h and distilled before use. 1,3-Butadiene and ethene were purchased from Società Ossigeno Napoli (SON) and used without further purification. Methylalumoxane was purchased by Witco and used as a solid after distillation of solvent. The catalysts, *rac*-[CH_2(3-*tert*-butyl-1-indenyl)$_2$]$ZrCl_2$ (I) [8] and *rac*-[CH_2(3-methyl-1-indenyl)$_2$]$ZrCl_2$ (II) [6] were synthesized using the procedures reported in the literature. Polymerization reactions were carried out at 50 °C in a 250 cm^3 glass autoclave, introducing 100 cm^3 of toluene and MAO, butadiene, and the catalyst, as reported in Tables 1 and 2. The autoclave was fed with ethene (5 atm) and kept under mechanic stirring over the runs. Then it was vented and the polymerization mixture was recovered by precipitation with ethanol/HCl, filtered, washed with an

Table 1
Polymerization conditions and microstructures of E–C3 copolymers

Run	Cat	[Zr] (mol/l)	[Al]/[Zr]	[B] (mol/L)	[E]/[B]	Time (min)	*T* (°C)	Yield (g)	B^a (mol %)	C3^a (mol %)	C5^a (mol %)
1	I	2.4×10^{-4}	300	0.65	2.5	120	20	31	0.39	0.29	0.10
2	I	1.1×10^{-4}	500	2.3	0.86	60	50	38	1.34	0.80	0.54
3	I	1.0×10^{-5}	1000	0.62	0.39	1080	20	0.8	4.0	2.68	1.32

[a] Copolymer constitutional units: (B) overall amount from butadiene; (C3) 1,2-cyclopropane units; (C5) 1,2-cyclopentane units, as determined by ^{13}C NMR [6].

Table 2
Polymerization conditions and microstructures of other ethene copolymers with 1,3-butadiene

Run	Cat	[Zr] (mol/l)	[Al]/[Zr]	[B] (mol/L)	[E]/[B]	Time (min)	T (°C)	Yield (g)	B[a] (mol %)	C5[a] (mol %)	1,3[a] (mol %)	1,1[a] (mol %)
4	II	2.3×10^{-5}	1000	0.55	1.58	50	50	50.1	2.5	2.5	–	–
5	II	2.3×10^{-5}	1000	1.38	0.64	20	50	35.1	6.4	6.4	–	–
6	I	8.3×10^{-4}	1000	0.52	0.09	90	73	0.40	5.6	–	1.3	4.3
7	I	8.3×10^{-4}	1000	8×10^{-3}	0.10	1500	50	0.55	2.6	–	0.9	1.7

[a] Copolymer constitutional units: (B) overall amount from butadiene; (C5) 1,2-cyclopentane units; (1,3) *trans*-1,3 units; (1,1) *trans*-1,1 units.

excess of ethanol and dried under reduced pressure at room temperature.

2.2. NMR measurements

^{13}C Nuclear magnetic resonance (NMR) spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz at 393 K. The samples were prepared by dissolving 40 mg of polymer in 0.5 cm^3 of tetrachlorodideuteroethane. Hexamethyldisiloxane was used as internal chemical shift reference. The resonances were assigned on the base of the data reported in the literature [4–6]. The percent amounts of ethene and butadiene (C3; C5; 1,1; 1,3 constitutional units of Scheme 1) in the copolymers were calculated by the method described in detail in Ref. [6].

Solid state ^{13}C NMR spectra were obtained at room temperature by a Bruker AVANCE 300 spectrometer operating at 75.47 MHz, in CP-MAS (cross-polarization, magic-angle spinning) mode. Samples were packed into a zirconia rotor and spun at the magic angle with a rotation spin of 5 kHz. In order to achieve stable spinning, fine NaCl powder was added to fill up the rotor. ^{13}C NMR spectra were acquired under proton decupling with a contact time of 1.5 ms. The spectra were recorded after 12000 scans, using an acquisition time of 45 ms with a delay of 5 s between the pulses. ^{13}C chemical shift were assigned using as reference the CH peak of 1,2-cyclopentane units (44.2 ppm) as seen in solution ^{13}C NMR spectra.

2.3. Thermal crosslinking

Before crosslinking procedures, the polymeric powders were shaped as ≈1 mm thick sheets, simply by compression at room temperature at a load of 5 metric tons. The crosslinking process was carried out by keeping these sheets at a constant annealing temperature (T_a) for a prescribed time, under nitrogen atmosphere, in a Mettler TG50 thermobalance.

2.4. Extraction procedures

The gel fraction has been determined, according to the ASTM method [23], as the percent of the original weight of the sample after extracting for 6 h in boiling decahydronaphthalene (decaline, a mixture of *cis* and *trans* isomers). The extraction has been followed by drying at 150 °C in a vacuum oven. As suggested by this standard method, to avoid polymer degradation during the extraction procedure, an antioxidant agent has to be used. In particular, 2,2′-methylene-bis-(4-methyl-6-tert-butyl phenol) was dissolved in decaline (1 wt%), before the extraction tests.

2.5. Molecular mass between crosslinks

The crosslinked networks have been characterized by the standard procedure involving swelling measurements

[24–25]. In particular, the molecular mass between crosslinks (M_c) has been evaluated for sample 2 by:

$$M_c = -\frac{[d_p V_o (V_p^{1/3} - V_p/2)]}{V_p + V_p^2 \chi + \ln(1 - V_p)}$$

where d_p is the measured polymer density, 0.91 g/cm^3.

V_o is the molar volume of solvent (for decahydronaphthalene $V_o = 144$ cm^3/mol).

χ is the polymer–solvent interaction parameter, which has been assumed equal to 0.025 that is an average between 0.03 (LDPE-*cis* decaline) and 0.02 (LDPE-*trans* decaline) [26].

V_p is the volume fraction of the polymer in networks swollen in decahydronaphthalene, determined from the weight of the dry (extracted) and swollen samples, assuming additivity of the volumes, by the following equations:

$$V_p = \frac{1}{1+Q} \quad \text{with} \quad Q = \frac{W_s}{W_p}\frac{d_p}{d_s}$$

where d_s is the density of the solvent (0.896 g/cm^3);

W_s is the solvent weight in the gel;

W_p is the polymer weight in the gel.

2.6. X-ray diffraction measurements

X-ray diffraction patterns have been obtained with an automatic 1710 Philips powder diffractometer using a Ni-filtered Cu Kα radiation. A crystallinity index has been obtained by resolving the X-ray diffraction patterns, for the range $10° < 2\theta < 40°$, into diffraction areas relative to the crystalline peaks and to the amorphous halo.

2.7. Calorimetric measurements

Calorimetric measurements have been carried out on a DSC 2920 apparatus manufactured by TA Instruments, in flowing N_2, with heating rate of 10 °C/min. The melting temperatures and the heats of fusion have been evaluated from the peak temperatures and the areas of the maxima of the appropriate endotherms. Before DSC measurement, the previous thermal history of the samples was erased by heating them up to 140 °C followed by cooling at a rate of 10 °C/min down to −150 °C, in the DSC apparatus, under nitrogen atmosphere.

2.8. Gel permeation chromatography (GPC)

The molecular weight distribution and polydispersity index were estimated by gel permeation chromatography at 140 °C using 1,2,4-trichlorobenzene as solvent and narrow molecular weight distribution polystyrene standard samples as reference. The measurements were performed on PL-GPC210 with 4 PL-Gel Mixed A Columns, refractive detector and DM400 datamanager (Viscotek).

3. Results and discussion

3.1. Polymerization tests and polymer microstructures

E–C3 copolymers. The polymerization conditions and the microstructure of the E–C3 copolymers which have been used in the present paper are listed in Table 1. All samples of Table 1 have been obtained by the catalytic system *rac*-[CH$_2$(3-*tert*-butyl-1-indenyl)$_2$]ZrCl$_2$(I)/MAO. For all samples the conversion of butadiene was less then 2% and the final products were random copolymers containing only isolated cyclic units. In fact we did not detect in the ^{13}C NMR spectra any signal at 15.1 and 38.2 ppm relative to methine and methylene groups of two adjacent cyclopropane units [6].

Other ethene copolymers with 1,3-butadiene. The polymerization conditions and the microstructure of other ethene copolymers with 1,3-butadiene, which have been used in the present paper, are listed in Table 2. Samples 4 and 5 have been obtained by the catalytic system *rac*-[CH$_2$(3-methyl-1-indenyl)$_2$]ZrCl$_2$(II)/MAO. Samples 6 and 7 have been obtained using the catalytic system *rac*-[CH$_2$(3-*tert*-butyl-1-indenyl)$_2$]ZrCl$_2$(I)/MAO.

All samples listed in Table 1 and Table 2 are characterized by high molecular masses, with weight average molecular weights in the range 2.5–6.5×10^5 uma.

3.2. Crosslinking and thermal treatments

The gel fractions as measured for the copolymer samples of Tables 1 and 2, after thermal treatments at 200 °C for 30 min,

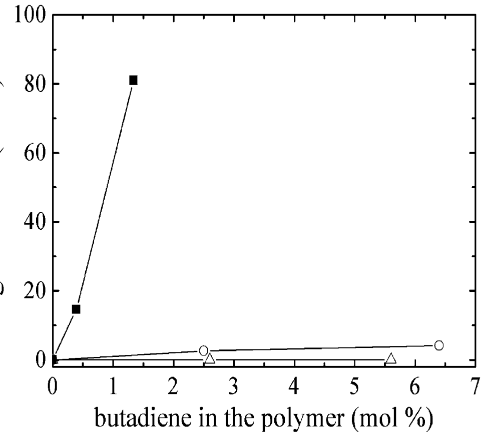

Fig. 1. Gel fractions measured for copolymer samples of Tables 1 and 2, after thermal treatments at 200 °C for 30 min. Open circles: copolymers containing only 1,2-cyclopentane units; open triangles: copolymers containing 1,1 and 1,3 butadiene units; solid squares: copolymers containing 1,2-cyclopropane units.

under nitrogen atmosphere, are reported in Fig. 1 versus the molar content of monomeric units from butadiene.

It is apparent that for the copolymers of Table 1, which include 1,3-butadiene prevailingly as methylene-1,2-cyclopropane units, quite large gel fractions are obtained. For instance, a nearly complete loss of solubility (gel fraction of 81%) is already reached for C3 content of 0.8 mol%. On the other hand, for the same thermal treatments on the copolymers of Table 2 which include 1,3-butadiene as different monomeric units (models B–D of Scheme 1), the gel fraction remains always smaller than 10%, also for molar content of comonomer units from butadiene as high as 6%.

These results clearly suggest that the occurrence of crosslinking is due to the presence of the cyclopropane rings along the copolymer chains.

Also informative are thermal crosslinking studies for a given copolymer sample by varying the temperature and time of the treatments. In particular, the gel fractions as measured for the copolymer sample 2 (Table 1, C3 content of 0.8 mol%), after thermal treatments for 55 min are reported in Fig. 2 versus the annealing temperature (T_a). It is apparent that up to $T_a = 140$ °C (i.e. well above the melting temperature of the starting polymer, $T_m \approx 115$ °C) the crosslinking is negligible while a nearly complete crosslinking (gel fraction of ≈83%) is already present for $T_a = 180$ °C.

The gel fractions and the molecular mass between crosslinks (M_c), measured for the same copolymer, after thermal treatments at $T_a = 200$ °C, are reported in Fig. 3 versus the annealing time. It is apparent that after 30 min of crosslinking, high gel fraction values (>80%) are already reached.

3.3. Crystallinity and melting behavior of crosslinked samples

The X-ray diffraction patterns and DSC scans of sample 2 before thermal crosslinking (a) and of its decaline-insoluble fraction after annealing at 200 °C for 55 min (b) are reported in Fig. 4A and B, respectively.

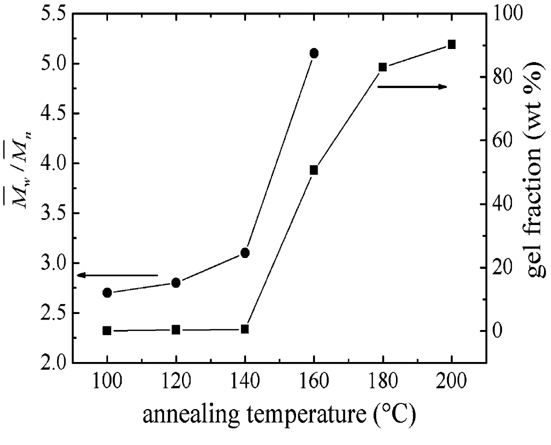

Fig. 2. Gel fractions (right scale) for the E–C3 copolymer sample 2 (Table 1, C3 = 0.8 mol%), after thermal treatments for 55 min, versus the annealing temperature. On the left scale the polydispersity ($\bar{M}_w/\bar{M}_n$) as measured for the decaline soluble fraction is also reported.

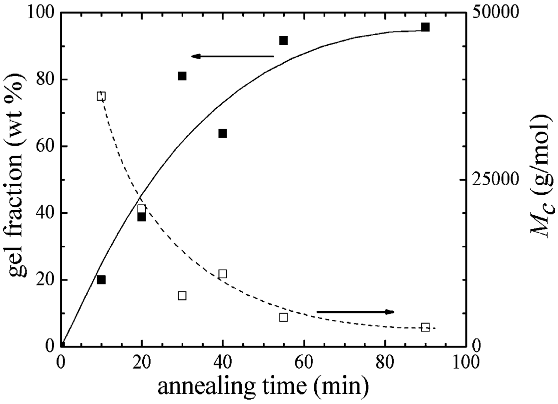

Fig. 3. Gel fractions and molecular mass between crosslinks (M_c) measured for the E–C3 copolymer sample 2, versus the annealing time for $T_a = 200$ °C.

The X-ray diffraction patterns remain essentially unaffected by the considered thermal crosslinking procedure, indicating that the occurrence of crosslinking does not hinder the copolymer crystallization.

The DSC scans of Fig. 4B show that the melting temperature ($T_m \approx 115$ °C) and the melting enthalpy ($\Delta H \approx 120$ J/g) are also essentially unaffected by the considered thermal crosslinking procedure.

3.4. GPC and NMR characterizations

Some information relative to the crosslinked network can be indirectly achieved by molecular characterization of the polymer fractions, which remain soluble after the crosslinking procedure. In particular, soluble fractions of samples annealed in different conditions have been characterized by high temperature GPC measurements as well as by ^{13}C NMR spectra.

GPC measurements on the soluble fractions of the E–C3 samples, after thermal crosslinking procedures indicate the occurrence of a significant increase of the broadness of the molecular weight distribution. Just as an example, the polidispersity index ($\bar{M}_w/\bar{M}_n$) of sample 2, after thermal treatments for 55 min at different temperatures is reported on the left scale of Fig. 2. It is clearly apparent that polydispersity remains nearly constant for thermal treatments up to 140 °C while it increases steeply for annealing at 160 °C. Correspondingly, the weight average molecular weight remains close to the starting value ($\bar{M}_w = 6.4 \times 10^5$ uma). Hence, the crosslinking reactions which occur for $T_a > 140$ °C not only produce insoluble fractions (Fig. 2, right scale) but also make broader the molecular weight distribution of the soluble fractions (Fig. 2, left scale).

The ^{13}C NMR spectra clearly indicate that the soluble fractions of the E–C3 samples, after the thermal

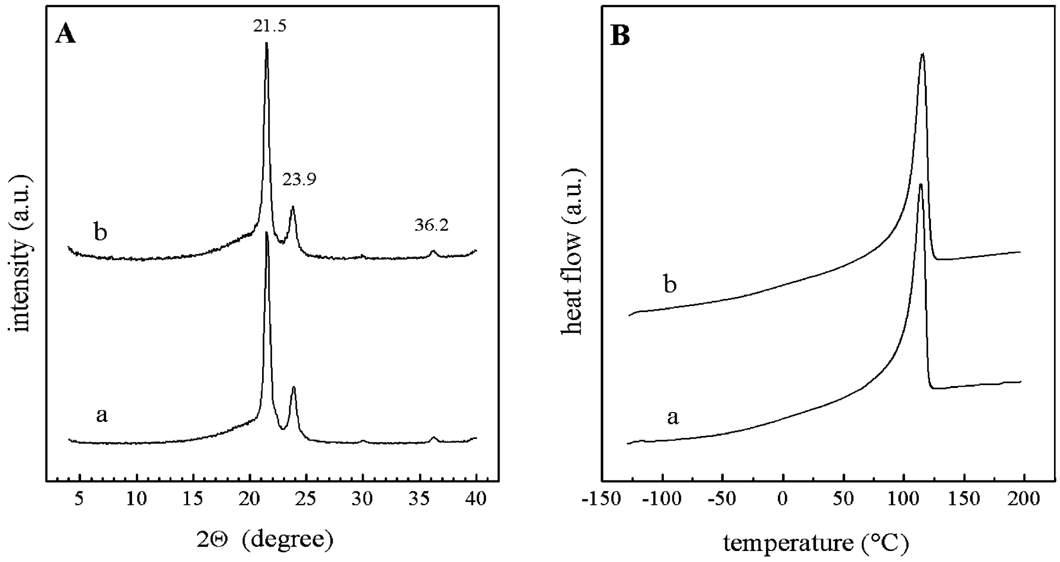

Fig. 4. X-ray diffraction patterns (A) and DSC scans (B) of the E–C3 copolymer sample 2 (C3 = 0.8 mol%): (a) before annealing; (b) after annealing at 200 °C for 55 min (decaline insoluble fraction).

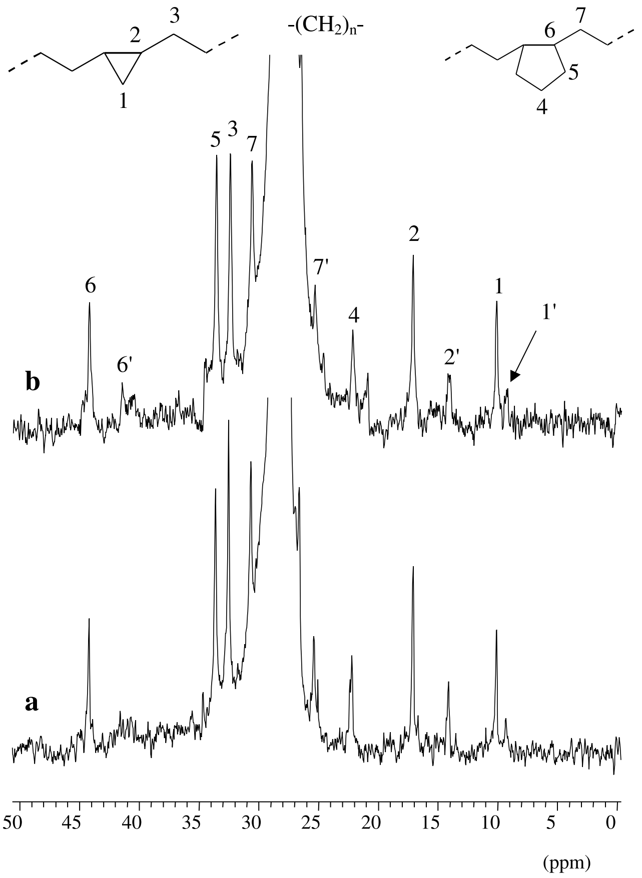

Fig. 5. ^{13}C NMR spectra of the E–C3 copolymer sample 2 (C3 = 0.8 mol%): (a) before annealing; (b) after annealing at 200 °C for 30 min (decaline soluble fraction). The minor peaks relative to carbons of cycloalkane rings in the cis configuration are labeled with prime number.

crosslinking procedures, present a C3/C5 ratio lower than the starting whole samples. This is, for instance, shown for sample 2, whose ^{13}C NMR spectrum is reported in Fig. 5a and compared with the spectrum of its soluble fraction ($\approx$20 wt%), after annealing at 200 °C for 30 min (Fig. 5b). A quantitative comparison shows that the soluble fraction presents a decrease of the intensity of the C3 peaks (1–3) of nearly 30%, while the C5 peaks (4–8) remain essentially unaltered. This is clearly shown also by a visual comparison of the heights of the resonances 3 and 5 in Fig. 5.

This kind of information has been also confirmed by solid state ^{13}C NMR measurements, which, due to their lower resolution, have been effected on a E–C3 copolymer having a larger content of monomeric units from butadiene (4 mol%, sample 3 of Table 1). Just as an example, the spectrum of the untreated sample and of the sample treated at 200 °C for 55 min have been compared in Fig. 6. In these spectra, due to the broadness of the very intense polyethene methylene resonance, only the resonances of carbons 1 and 2 of the C3 units and carbon 6 of the C5 units are well resolved. However, it is clearly apparent that the used crosslinking procedure leaves unaltered the C5 signal while both C3 signals are reduced of nearly 20%.

Both high resolution ^{13}C NMR spectra of soluble fractions and ^{13}C NMR solid state spectra of insoluble fractions do not show the appearance of new resonances, which could in principle give some information relative to the chemical structure of the crosslink points. This was expected due to the considerably high molecular weights of the starting materials. In fact, in order to get this microstructural information, much lower molecular weights of the starting polymer (e.g. $\bar{M}_w < 10^4$ uma) would be needed, as reported for radiation-induced [16] and photo-initiated [13] polyethene crosslinking.

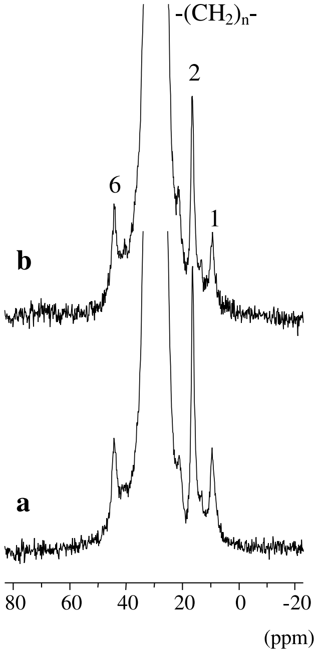

Fig. 6. Solid state ^{13}C NMR spectra of the E–C3 copolymer sample 3 (C3 = 2.7 mol%): (a) before annealing; (b) after annealing at 200 °C for 55 min. The numerical labels of the resonances are defined by the inset structures of Fig. 5.

4. Conclusions

Ethene/1,3-butadiene copolymers, which include 1,3-butadiene prevailingly as methylene-1,2-cyclopropane units, are easily crosslinked by thermal treatments in the temperature range 160–200 °C. In fact, a nearly complete loss of solubility can be easily reached also for copolymers with C3 content as low as 0.8 mol% while for copolymers including 1,3-butadiene as different constitutional units (models B–D of Scheme 1), for the same thermal treatments, the gel fractions remain small. These results clearly suggest that the occurrence of crosslinking is due to the presence of the cyclopropane rings along the copolymer chains. This hypothesis is confirmed by ^{13}C NMR spectra on polymer fractions which remain soluble after the crosslinking procedures as well as by solid state NMR spectra of insoluble fractions, indicating a reduced C3 content, and unaltered C5 content, with respect to the untreated samples.

The reported results indicate that for the E–C3 copolymer with a C3 content of 0.8 mol%, up to $T_a = 140$ °C (i.e. well above of its melting temperature, $T_m \approx 115$ °C) the crosslinking is negligible while a nearly complete crosslinking is already present for $T_a = 180$ °C. Moreover, as suitable for XLPE materials, polymer melting temperature and degree of crystallinity remain essentially unaffected by the considered thermal crosslinking procedures.

In this respect, it is worth noting that typical gel fractions of commercial XLPE samples are in the range 40–80% and that typical moulding temperatures are in the range 120–140 °C while crosslinking temperatures are in the range 180–230 °C [27]. Hence, it is possible to conclude that gel fraction and crystallinity typical of commercial XLPE can be easily reached for E–C3 copolymers, for thermal treatments in conditions which can be compatible with industrial fabrication processes.

Acknowledgements

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[22] As for the latter copolymer it is worth noting that the insertion of butadiene as 1,2-cyclopentane ring units, by suitable metallocene-catalyzed copolymerizations with ethene, was described several years ago by (a) Galimberti M, Albizzati E, Abis L, Bacchilega G. Makromol Chem 1991;2591:192. (b) Welborn Jr HC. Eur Pat EP0275676; 1988. Chem Abstr 1988;109:150259z. However, these copolymers insert most butadiene as *trans*-1,4 units while only recently, the achievement of ethene copolymers including butadiene essentially only as 1,2-cyclopentane ring units has been described [6].
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