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Infrared spectra and thermal reactivity of ethene copolymers containing 1,2-cyclopropane units

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Abstract

A comparison between ^{13}C NMR spectra of polymer solutions and Fourier transform infrared spectra of polymer films for several ethene–butadiene copolymers, including most butadiene as 1,2-cyclopropane and 1,2-cyclopentane units, is presented. This spectral comparison, also with the help of a low-molecular-mass model compound specifically synthesized for this purpose, has allowed to locate infrared absorbances associated with the cyclic comonomer units. In particular, a satisfactory calibration curve for evaluation of the amount of the reactive cyclopropane units, from the absorbance of the 1020 cm^{-1} band, has been achieved. An analysis of 1,2-cyclopropane unit reactivity in annealed films, has also pointed out that the presence of remnants of the polymerization catalyst can produce large increase in cyclopropane reactivity.
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Keywords: Ethene–butadiene copolymers; Cycloalkane infrared absorbances; 1,2-Cyclopropane reactivity

1. Introduction

In recent works 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 [1–3], catalyzed by the highly sterically hindered metallocene *rac*-[CH$_2$(3-*tert*-butyl-1-indenyl)$_2$]ZrCl$_2$, discovered by Resconi and coworkers [4].

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 (C3, in Scheme 1A) together with methylene-1,2-cyclopentane units (C5 in Scheme 1B), in a ratio generally not far from 2:1 and both with high trans selectivity [1–3].

These new ethene copolymers (hereafter cited as E-C3 copolymers), could be in principle relevant since are obtained with high yields from basic monomers and since contain a controlled number of reactive cyclopropane rings. In particular, it has been recently pointed out that E-C3 copolymers lead to crosslinked polyethene (XLPE) by simple thermal treatments in conditions which appear to be suitable for industrial fabrication processes [5].

The molecular structure of E-C3 copolymers has been thoroughly characterized in solution, by ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy. Variations of molecular structure of the crosslinked insoluble polymers (obtained from E-C3 copolymers by thermal treatments) have been studied by solid state ^{13}C NMR spectroscopy, in CP-MAS (cross-polarization, magic-angle spinning) mode [5]. However, as usual, the accuracy of quantitative evaluations based on this solid state technique is rather poor.

In this note we present a comparison between ^{13}C NMR spectra of polymer solutions and Fourier transform infrared (FTIR) spectra of polymer films, for several E-C3 copolymers as well as for copolymers with only 1,2-cyclopentane units [3]. This comparison has also included the ethene homopolymer obtained by the same catalytic system as well as a low-molecular-mass model compound (1,2-di-*n*-hexyl-cyclopropane shown in Scheme 1C), specifically synthesized for this purpose.

This analysis has shown that simple FTIR measurements on polymer films can afford accurate evaluation of the cyclopropane unit content, through a simple calibration curve. Of course, the FTIR technique beside the usual advantages of fast sampling rate gives also the opportunity to get simple in situ studies of reactions of E-C3 copolymers leading to insoluble products.

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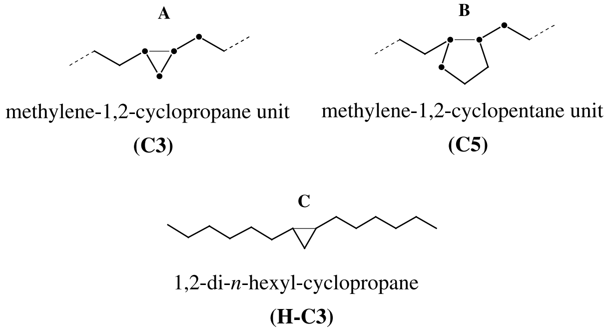

Scheme 1. Constitutional units in ethene–butadiene copolymers and the low-molecular-mass model compound.

2. Experimental section

2.1. Polymerization conditions and polymer characterization

Polymerization conditions and microstructures of the copolymers which have been used in the present paper are listed in Table 1. The homopolymer sample **1** and the copolymer samples **2–6**, which include both C3 and C5 units, were obtained by the catalytic system *rac*-[CH_2(3-*tert*-butyl-1-indenyl)$_2$]$ZrCl_2$(**I**)/MAO; the ethene copolymer including only C5 units (sample **7**) has been obtained with the less hindered catalytic system *rac*-[CH_2(3-metyl-1-indenyl)$_2$]$ZrCl_2$(**II**)/MAO. All samples listed in Table 1 are characterized by high molecular masses, with weight average molecular weights in the range $2.5–6.5\times10^5$ u.m.a.

Polymerization reactions were carried out, in toluene solutions by using the monomer and catalyst concentrations reported in Table 1. The obtained polymers were coagulated by pouring the reaction mixture into acidified ethanol, filtered, washed with further ethanol and then dried under reduced pressure at room temperature.

Generally the reaction vessel was a 1 L glass autoclave fed with a constant ethene overpressure (3 atm for run **6**; 6 atm in the other cases) and kept under mechanical stirring over the run. E-C3 copolymer samples **4** and **5** were instead obtained in a 100 mL glass flask magnetically stirred and thermostated at 20 °C, charged sequentially with toluene (10 mL), MAO and 1,3-butadiene. Then ethene was introduced into reactor at a constant pressure of 1 atm and the polymerization was started by introducing 2 mL of a toluene solution of the zirconocene.

2.2. Synthesis of the low-molecular-mass model compound (1,2-di-n-hexyl-cyclopropane)

The synthesis was carried out in analogy to the procedure described in [6] for the synthesis of *n*-decyl-cyclopropane. In a three necked round bottom flask, equipped with a stirring bar and a condenser and containing dry CH_2Cl_2 (200 mL), 20 g (0.10 mol) of 7-tetradecene and 41.54 g (0.15 mol) of di-iodomethane were added. The mixture was cooled at 0 °C, then 78 mL of an $Al(C_2H_5)_3$ solution (2 M in hexane) were added dropwise to the solution, stirring vigorously. The solution was stirred for 24 h at room temperature. Then it was diluted with CH_2Cl_2 (200 mL) and 21.71 g (0.52 mol) of NaF were added.

The mixture was cooled at 0 °C and water (25–30 mL) was added dropwise with caution. The system was allowed to warm at room temperature and stirred vigorously for other 30 min. The organic phase was extracted with CH_2Cl_2, dried over Na_2SO_4, and filtered. The solution was evaporated under reduced pressure, to remove CH_2Cl_2, obtaining an oily liquid (20.3 g, yield close to 100%).

2.3. NMR measurements

Nuclear magnetic resonance (NMR) spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz at 373 K. Samples were examined as solutions in 1,1,2,2-tetrachlorodideuteroethane (generally 40 mg in 0.5 cm^3). Hexamethyldisiloxane was used as internal chemical shift reference. As for 1,2-di-*n*-hexyl-cyclopropane, all resonances have been assigned as carbons of *trans* and *cis* isomers:

trans-isomer: 10.05 ppm CH_2-cycle (1); 17.07 ppm CH-cycle (2); 32.44 ppm α-CH_2 (3); 27.57 ppm β-CH_2; 27.25 ppm γ-CH_2; 20.67 ε-CH_2; 11.94 ppm ζ-CH_3;

cis-isomer: 9.23 ppm CH_2-cycle (1); 14.12 ppm CH-cycle (2); 28.21 ppm α-CH_2 (3); 26.84 ppm β-CH_2; 27.25 ppm γ-CH_2; 20.67 ε-CH_2; 11.94 ppm ζ-CH_3.

Greek letters refer to those indicated in Fig. 1D.

As for polymer samples, the resonances were assigned on the basis of the data reported in the literature [1–3]. The percent amounts of ethene and butadiene (C3 and C5 constitutional units) in the copolymers were calculated by the method described in detail in [3].

Table 1
Polymerization conditions and polymer microstructures

Run	Cat	[Zr]	[Al]/[Zr]	[B]	[E]/[B]	*T* (°C)	*t* (h)	Yield (g)	C3[a] (mol%)	C5[a] (mol%)
1	I	3.5×10^{-4}	1000	–	–	20	2	42.3	0	0
2	I	2.4×10^{-4}	300	0.65	2.64	20	2	31.0	0.23	0.17
3	I	1.1×10^{-4}	500	2.30	0.86	50	1	38.0	0.80	0.54
4	I	8.1×10^{-4}	1000	0.52	0.46	20	2	1.2	1.05	0.53
5	I	4.4×10^{-4}	500	0.60	0.40	20	3	1.3	1.27	0.63
6	I	1.3×10^{-4}	1000	4.20	0.22	20	4.5	2.3	1.95	1.1
7	II	2.3×10^{-5}	1000	1.38	0.64	50	0.3	35.1	0	6.4

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

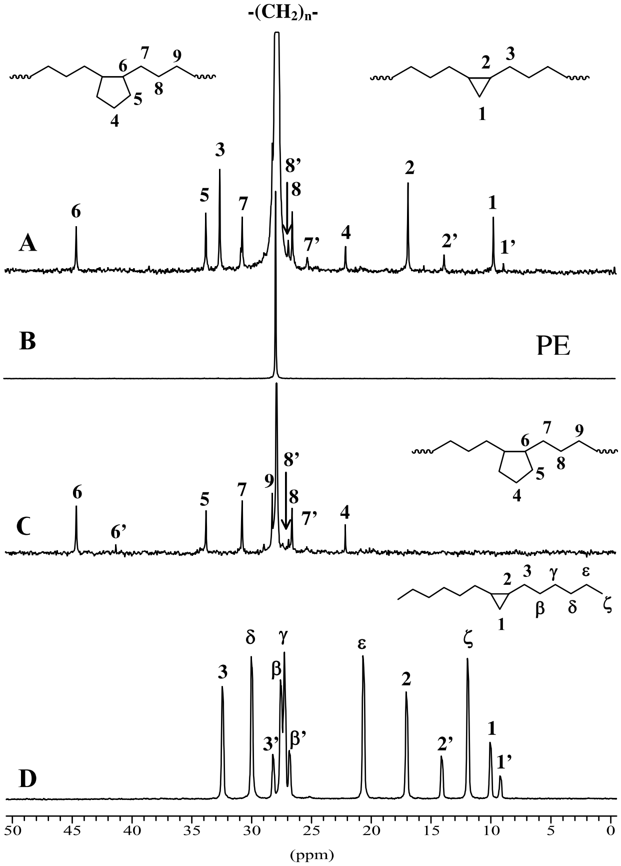

Fig. 1. Aliphatic region of ^{13}C NMR spectra of solutions of: A copolymer containing 1.27 mol% C3 and 0.63 mol% C5; B polyethene; C copolymer containing only C5 units (6.4 mol%); D 1,2-di-*n*-hexyl-cyclopropane. For the sake of comparison, peak 1 (for A and D) and peak 4 (for A and C) have been plotted with the same height. Primed numbers are referred to *cis*-isomers.

2.4. Film preparation procedure

The films used for FTIR measurements have been prepared by compression moulding procedure at 135 °C. This temperature is above the polymer melting temperature but below the minimum temperature of significant crosslinking. In fact, in a previous paper [5] we have shown that crosslinking of E-C3 copolymers is negligible for annealing below 140 °C.

The polymer samples including catalyst remnants, used for the annealing studies of Figs. 4–6, have been prepared by compression of fine powders at room temperature, under a load of 5 metric tons.

2.5. FTIR measurements

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 Bruker spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He–Ne reference laser. Thirtytwo scans were signal averaged to reduce the noise. The thickness of films used for infrared measurements was always comprised between 100 and 200 μm, in order to keep the peaks of interest in the range of absorbance–concentration linearity.

3. Results and discussion

3.1. NMR spectra

The aliphatic region of the ^{13}C NMR spectra of a E-C3 copolymer (sample 5 of Table 1), of a polyethene sample obtained by the same catalytic system (sample 1 of Table 1), of a E-C5 copolymer (sample 7 of Table 1) and of the low molecular mass model compound (1,2-di-*n*-hexyl-cyclopropane) are compared in Fig. 1A–D, respectively.

As described in a previous report [1], these E-C3 copolymers show only very weak (if any) signals in the region of the unsaturated carbons, while the aliphatic region includes, beside the intense signal placed at 27.8 ppm related to methylene sequences (Fig. 1B) and beside the five resonances of *trans*-1,2-disubstituted and minor resonances of *cis*-1,2-disubstituted cyclopentane units [7] (clearly pointed out by the spectrum of Fig. 1C), several additional resonances which have been attributed to 1,2-disubstituted cyclopropane rings. In particular, three resonances placed at 10.1, 17.1 and 32.5 ppm have been attributed to *trans*-1,2-disubstituted cyclopropane rings while the minor resonances at 9.3 and 14.1 ppm have been attributed to *cis*-1,2-disubstituted rings ($1'$ and $2'$ in Fig. 1).

It is worth adding that the trans/cis ratio, being close to 3 for the low-molecular-mass compound, is generally larger than 4 for the obtained E-C3 copolymers.

Quantitative evaluations of the molar content of cycloalkane units for all prepared copolymers, based on ^{13}C NMR spectra like that one of Fig. 1A, are listed in columns 10, 11 of Table 1.

3.2. FTIR spectra

FTIR spectra for the spectral range 3500–600 cm^{-1}of films prepared with the same samples of Fig. 1A–D are shown in Fig. 2A–D, respectively. For these spectra, the regions 3100–2900 cm^{-1} and 1200–800 cm^{-1} have been expanded in the upper and lower part of Fig. 2, respectively.

As for the E-C3 copolymers (Fig. 2A), it is apparent that, beside the usual polyethene absorbances (Fig. 2B), there are several weak absorbances (at 3057, 2988, 1020, 966 and 908 cm^{-1}), which could be attributed to vibrational modes of the cyclic comonomer units. In particular, a comparison between the spectra of Fig. 2 immediately indicates that the C–H stretching bands at 3057 and 2988 cm^{-1} (being present in A and D but not in C) have to be attributed to the C3 units.

The attribution of the absorbances in the more complex spectral region 1200–800 cm^{-1} requires a more detailed spectral analysis (lower part of Fig. 2). A difference spectrum obtained by subtraction of the spectrum C (E-C5 copolymer) from the spectrum A (copolymer with C3 and C5) has been reported as curve E in the lower part of Fig. 2. This difference spectrum, which should correspond in principle to the spectrum of C3 units, is indeed very similar to spectrum of the model C3 compound (curve D).

Hence, the spectra and the spectral difference of Fig. 2 clearly indicate that the 966 cm^{-1} absorbance has to be mainly

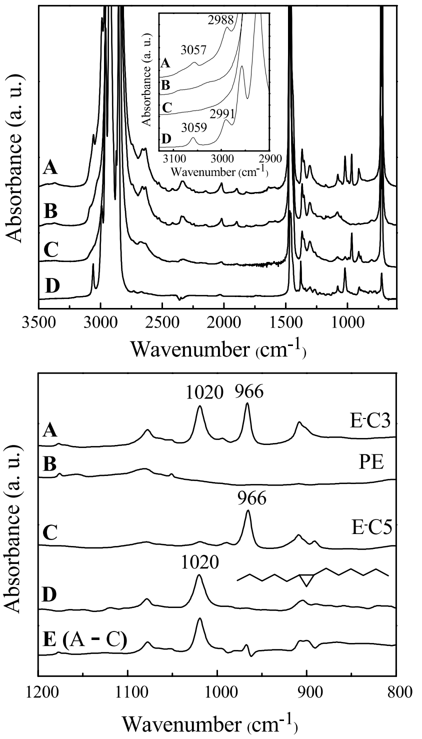

Fig. 2. FTIR spectra for different spectral ranges of: A copolymer containing 1.27 mol% C3 and 0.63 mol% C5; B polyethene; C copolymer containing only C5 units (6.4 mol%); D 1,2-di-*n*-hexyl-cyclopropane. For the enlarged spectral range 1200–800 cm^{-1}, also the difference spectrum between A and C has been reported (E). For the sake of comparison, the 1020 cm^{-1} band has been plotted with a same intensity for spectra A, D and E while the 966 cm^{-1} band has been plotted with a same intensity for spectra A and C.

attributed to the C5 units, because this band is intense for A and C spectra, but absent in D and E spectra. On the other hand, the 1020 cm^{-1} absorbance is mostly due to the C3 units because it is the most intense band of spectra D and E while it is very weak for the spectrum C.

A detailed analysis of the absorbance has shown that the vibrational band most suitable for the evaluation of the content of C3 units is the 1020 cm^{-1} band. In fact, for all the considered E-C3 copolymers of Table 1, the absorbance of this band (normalized with respect to the film thickness) has been reported in Fig. 3 versus the C3 unit molar content, as evaluated by solution ^{13}C NMR spectra. The plot of Fig. 3 can be considered a satisfactory calibration curve for a solid-state and fast evaluation by FTIR technique of the molar content of the reactive cyclopropane units.

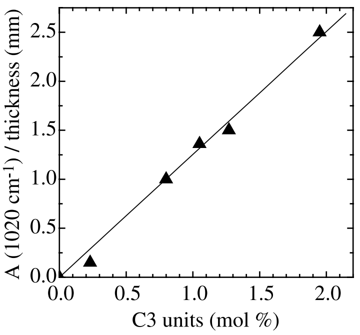

Fig. 3. Calibration line relating, for E-C3 copolymer films, the normalized absorbance of the cyclopropane vibrational peak at 1020 cm^{-1} with the cyclopropane units molar content.

Our analysis has also shown that the 966 cm^{-1} band, mostly due to cyclopentane units, cannot be used for quantitative evaluations of the amount of these comonomeric units, possibly due to its superposition with the absorbance of *trans*-vinylene groups –CH=CH– [8–10].

3.3. FTIR study of high-temperature reactivity of cyclopropane rings

On the basis of the previous analysis, and in particular on the basis of the calibration line of Fig. 3, the FTIR technique allows an easy ‘in situ’ study of the cyclopropane reactivity in films crosslinked by high temperature annealing procedures. In particular, for the E-C3 copolymer with 1.27 mol% of cyclopropane units (sample 5 of Table 1), FTIR spectra for the spectral range 1150–1000 cm^{-1} before (A) and after 1 h of thermal treatment at 200 °C (under nitrogen atmosphere) (B) are shown in Fig. 4a. The reduction of the absorbance of the 1020 cm^{-1} band (13%) indicates a reduction of C3 molar content (compatible with that one measured on the basis of solid-state NMR measurements) [5].

Our FTIR analysis on annealed E-C3 copolymer samples has also pointed out that the presence of remnants of the polymerization catalyst (aluminoxane and metallocene) can have a strong influence on C3 reactivity. In particular, for the same E-C3 copolymer with 1.27 mol% of cyclopropane units and in the presence of 7 wt% of catalyst remnants, FTIR spectra before (curve A) and after thermal treatment at 200 °C for 1 h (curve B) and 4 h (curve C) are shown in Fig. 4b. By a comparison between the spectra of Fig. 4a and b, it is clearly apparent that thermal treatments, in the presence of catalyst remnants, more drastically reduce the absorbance of the 1020 cm^{-1} band. In particular, based on the calibration line

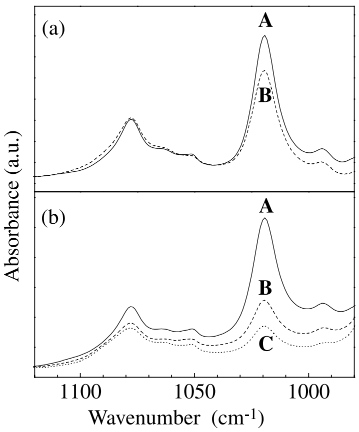

Fig. 4. FTIR spectra of the ethene copolymer with 1.27 mol% of cyclopropane units (sample 5 of Table 1) for the spectral range 1120–980 cm^{-1}, in the absence of catalyst remnants (a) or in the presence of 7 wt% of catalyst remnants (b): before (A), after 1 h (B) and after 4 h (C) of thermal treatment at 200 °C (under nitrogen atmosphere).

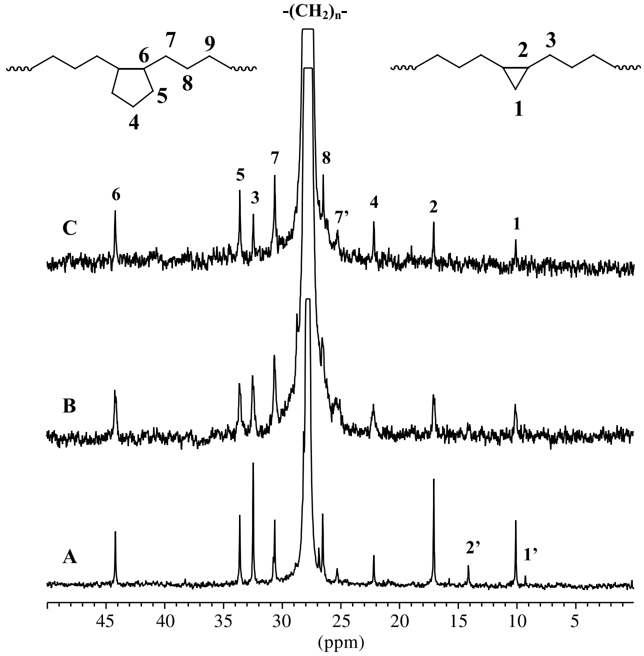

Fig. 5. A–C ^{13}C NMR spectra of the soluble fractions of the samples, whose FTIR spectra have been reported in Fig. 4B by curves A–C, respectively: unannealed sample (A); samples annealed at 200 °C in the presence of 7 wt% of catalyst remnants for 1 h (B) and for 4 h (C). The strong reduction of the cyclopropane signals (e.g. 3) with respect to the cyclopentane rings (e.g. 5 and 7) is clearly apparent.

of Fig. 3, the C3 concentration would be reduced of 66 and 83%, for the 1 and 4 h treatments, respectively.

These quantitative evaluations are compatible with ^{13}C NMR spectra (Fig. 5A–C) of the sample fractions remaining soluble after the annealing procedures (70–80 wt%), whose FTIR spectra have been reported in Fig. 4b by curves A–C, respectively. In fact, the reduction of the signals (1,2 and 3) of the cyclopropane units as measured for the soluble fractions of the films annealed at 200 °C for 1 h (Fig. 5B) and 4 h (Fig. 5C), indicate fractions of reacted C3 units of 55 and 77%, respectively.

Additional experiments have been conducted by annealing E-C3 copolymer samples into the FTIR apparatus, by increasing temperature from 30 °C up to 250 °C (step increase in 10 °C), with an annealing time of 15 min for each temperature. The percent of reacted cyclopropane units, evaluated on the basis of variations of the absorbance of the 1020 cm^{-1} band, for the E-C3 sample with 1.05 mol% of C3 units (sample 4 of Table 1), in the presence 0% and 50 wt% of catalyst remnant, are reported in Fig. 6A and B, respectively. The results of Fig. 6 indicate that the fraction of C3 units reacted after the successive thermal treatment up to 250 °C is close to 20 and 100% for samples containing 0% and 50 wt% of catalyst remnants, respectively.

4. Conclusions

Ethene–butadiene copolymers, with most butadiene inserted as methylene-1,2-cyclopropane and methylene-1,2-cyclopentane units, with molar content in the ranges 0.2–2.1 and 0.1–1.1%, respectively, have been characterized by ^{13}C NMR spectra of polymer solutions and by FTIR spectra of polymer films. These spectra have been compared with that one of the ethene homopolymer, obtained by the same catalytic system and with those of ethene–butadiene copolymers presenting only methylene-1,2-cyclopentane units. The spectral comparison has been extended to a low-molecular-mass model compound, including a cyclopropane ring in a *n*-alkane chain (1,2-di-*n*-hexyl-cyclopropane) specifically synthesized for this purpose.

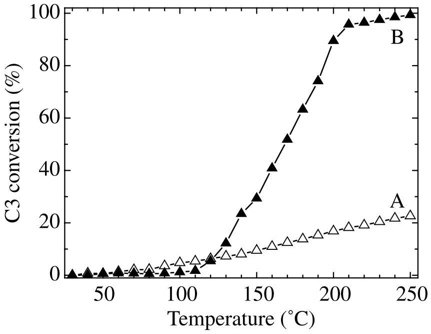

Fig. 6. Percent of reacted cyclopropane units, evaluated on the basis of variations of the absorbance of the 1020 cm^{-1} band, for the ethene copolymer sample with 1.05 mol% of C3 units (sample 4 of Table 1), in the absence (A, open triangles) or in the presence of 50 wt% (B, solid triangles) of catalyst remnants. The annealing has been conducted by increasing temperature from 30 °C up to 240 °C (step increase in 10 °C), with an annealing time of 15 min for each temperature.

These spectral comparisons have allowed to locate vibrational bands associated with cyclopentane (at 966 cm^{-1}) and cyclopropane (at 3057, 2988 and 1020 cm^{-1}) comonomeric units. More specifically, our analysis has shown that the vibrational band most suitable for the evaluation of the content of cyclopropane units is the 1020 cm^{-1} band and a satisfactory calibration curve for a solid-state and fast FTIR evaluation of the molar content of the reactive cyclopropane units has been achieved.

Our FTIR analysis on annealed E-C3 samples has also pointed out that the presence of remnants of the polymerization catalyst (aluminoxane and metallocene) can have a strong influence on C3 reactivity. In particular, the fraction of C3 units reacted after the thermal treatments at high temperatures (in the range 200–250 °C) which is close to 20% in the absence of catalyst remnants can increase up to nearly 80 and 100% for samples containing 7% and 50 wt% of catalyst remnants, respectively.

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