

Accepted Manuscript

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PII: S0014-3057(16)31231-9
DOI: <http://dx.doi.org/10.1016/j.eurpolymj.2017.01.010>
Reference: EPJ 7671

To appear in: *European Polymer Journal*

Received Date: 3 October 2016
Revised Date: 20 November 2016
Accepted Date: 8 January 2017

Please cite this article as: Estan-Cerezo, G., Alonso, D.A., Miguel Martín-Martínez, J., Reactivity of novel ethyl cyanoacrylate and 6-hydroxyhexyl acrylate adhesive mixtures and their influence on adhesion and thermal stability, *European Polymer Journal* (2017), doi: <http://dx.doi.org/10.1016/j.eurpolymj.2017.01.010>

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**REACTIVITY OF NOVEL ETHYL CYANOACRYLATE AND 6-HYDROXYHEXYL
ACRYLATE ADHESIVE MIXTURES AND THEIR INFLUENCE ON ADHESION AND
THERMAL STABILITY**

Gabriel Estan-Cerezo^{1,2}, Diego A. Alonso^{2}, José Miguel Martín-Martínez^{1*}*

¹Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain

*²Organic Chemistry Department and Institute of Organic Synthesis, University of Alicante, 03080 Alicante,
Spain*

*Correspondence to: Diego Alonso: Phone/Fax no. +34965909841; e-mail: diego.alonso@ua.es.

José Miguel Martín-Martínez: Phone no. +34965903977; Fax no. +34965909416;
e-mail: jm.martin@ua.es

ABSTRACT

Different amounts (5-10wt %) of an acrylate compound - 6-hydroxyhexyl acrylate (HHA) - was added to ethyl cyanoacrylate (ECN) for decreasing its stiffness and improving its thermal stability without decreasing its adhesion properties. The addition of HHA increased the immediate adhesion and decreased noticeably the glass transition temperature of the ECN. No reaction between HHA and ECN was observed in the ECN+HHA mixtures stored at 8 °C during long periods of time, but after 192 days a copolymerization by transesterification reaction between ECN and HHA was observed. The copolymerization of ECN and HHA produced new structures with broader molecular weight distribution and different tacticity than the ones obtained in the polymerization of ECN only. Because of the differences in structure, noticeable changes in the adhesion, structural, and thermal properties of the ECN+HHA polymers were observed. Whereas the ECN polymer decomposed at 200 °C, the copolymers of ECN+HHA decomposed near 300 °C.

Highlights:

- The addition of HHA increases the immediate adhesion of ECN.
- HHA decreases the stiffness and improves the thermal stability of ECN.
- Copolymerization between HHA and ECN is produced after long periods of time.

Keywords: cyanoacrylate, polymer synthesis, stability, tacticity

1. INTRODUCTION

Cyanoacrylates [1,2] are considered the most important instant adhesives and they have a range of applications in the automotive industry,[3] in revealing fingerprints,[4] and in medicine, among other.[5] Furthermore, cyanoacrylate polymers have been recently used in drug delivery system because of their ability to degrade with time.[6]

The properties of the cyanoacrylates are mainly determined by the mechanism of polymerization of the monomer. Thus, depending on the reaction conditions, the polymerization of the cyanoacrylates takes place through three mechanisms: anionic,[7] zwitterionic,[8] and radical.[9] Anionic polymerization of the cyanoacrylates is the most studied mechanism and it is initiated by inorganic bases such as water,[10] alcohols,[11] or blood.[12] While the zwitterionic polymerization of the cyanoacrylates can be initiated with neutral nucleophiles, such as tertiary amines or phosphines, the radical polymerization requires a radical initiator, such as azobisisobutyronitrile [9] or peroxides such as benzoyl peroxide.[13]

Cyanoacrylate polymers have some limitations derived from their high stiffness and relatively poor stability at high temperature. For improving these limitations, the addition of different compounds have been proposed.[14] For reducing the stiffness of the cyanoacrylate polymers, the addition of 2-methoxycarbonyl acrylic acid (ECA) (Figure 1) to ECN was proposed elsewhere,[15] and it was found that the glass transition temperature of the ECN+ECA polymers linearly decreased by increasing the ECA content. Furthermore, during polymerization lower degree of conversion of the cyanoacrylate monomer was observed by increasing the ECA

content. As a consequence, the ECN+ECA polymers showed lower stiffness than the ECN polymer, but the adhesion of ECN monomer was significantly decreased.

Several additives have been proposed for improving the thermal stability of the cyanoacrylate polymers.[16] Samatha *et al.*[17] added various acrylates for improving the thermal stability and the adhesion properties of cyanoacrylates. They found that the addition of 10 wt% of ethyleneglycol diacrylate (Figure 1) increased the adhesive strength of ethyl cyanoacrylate after being heated at 75-100 °C for 24 hours. Similar results were obtained by adding 15 wt% of methyl methacrylate (Figure 1). Samatha *et al.* [17] justified the improvement in the thermal stability by a cross-linking of the ECN and the acrylate monomer, and they were more marked in di-acrylates than in mono-acrylates. On the other hand, good storage stability at 25 °C was observed for all ECN+acrylate mixtures.

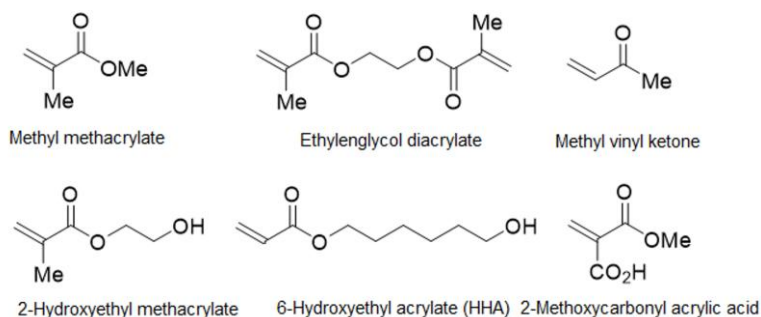


Figure 1. Chemical structure of acrylate derivatives.

On the other hand, Maruyama *et al.*[18] added methyl vinyl ketone to ECN (Figure 1) for improving the heat resistance of ECN polymerized with water, but a decreasing in adhesion was obtained. Furthermore, Han and Kim [9] have prepared several copolymers of ECN and methyl methacrylate (MMA) with enhanced thermal stability due to their alternating random distribution and the presence of stable MMA unit near the end of the copolymer chains.

While the influence of the addition of acrylates in the polymerization of cyanoacrylates has been studied in the past, the use of functionalized acrylates has been barely studied. In fact, Samatha *et al.*[17] have demonstrated that the addition of 5 to 20 wt% of 2-hydroxyethyl methacrylate (Figure 1) increased the adhesion of ECN adhesive, due to the cross-linking

between the monomer and the functionalized acrylate, involving the hydroxyl group of the acrylate as nucleophile in the reaction. On the other hand, in the patent by Martín-Martínez *et al.*[19] it has been evidenced a reduction in the heat of polymerization of the ECN by adding different amounts (5 to 20 v/v%) of acrylic derivatives such as 6-hydroxyhexyl acrylate (HHA) and alcoxycarbonyl acrylic acid (ECA) (Figure 1), but an important decrease in the adhesion of the ECN/alcoxycarbonyl acrylic acid (20 v/v%) mixture has been also observed. On the other hand, the mixtures of ECN and HHA have shown loss of stability after three weeks of storage at room temperature, but the stability of the ECN+HHA and ECN+ECA mixtures stored at 6-8 °C for three weeks was good.

Although the patent by Martín-Martínez *et al.*[19] proposed the addition of HHA to ECN, the adhesion and thermal properties of the polymers prepared with mixtures of ECN and different amounts of HHA has not been studied in detail yet, nor the variation of their properties with time. On the other hand, the evidences and mechanisms of the reaction of ECN and HHA with time have not been disclosed yet. Therefore, in this study the thermal properties and stability over the time of the polymers prepared with ECN and different amounts of HHA (5-10 v/v%) using a tertiary amine as catalyst, were studied and the adhesion of the ECN+HHA mixtures was monitored over the time. Furthermore, the structure of the copolymers obtained by reaction of HHA and ECN was studied.

2. EXPERIMENTAL

2.1. Materials

Triethylamine (Sigma Aldrich, San Louis, USA) was used as polymerization initiator. Ethyl cyanoacrylate (ECN) was provided by Adhbio S.L. (Elche, Spain). 6-Hydroxyhexyl acrylate (HHA) was synthesized from 1,6-hexanediol and acryloyl chloride, following the procedure reported by Alconcel *et al.*[20]

2.2. Preparation and polymerization of the ECN+HHA mixtures

Two mixtures containing 5.7 and 10 v/v% of HHA in ECN were prepared and stored in opaque glass vials at 6-8 °C in the fridge for avoiding deterioration by light exposure.

The polymerization of the ECN and the ECN+HHA mixtures was carried out by drop-wise addition of 1 v/v% aqueous (ultrapure water) triethylamine solution over 1 ml of the mixture placed in an aluminum container under continuous stirring, allowing to react for one hour. The resulting polymer was washed several times with ultrapure water to remove the non-reacted initiator, and afterwards the polymers were allowed to dry at room temperature for 48-72 hours.

2.3. Experimental techniques

Infrared spectroscopy (ATR-IR). The chemical composition of the ECN and ECN+HHA mixtures was determined by IR spectroscopy in Bruker Tensor 27 spectrometer (BrukerOptik GmbH, Ettlingen, Germany) working in the attenuated total reflectance mode (ATR); a diamond prism was used. The ATR-IR spectra were obtained by using an incidence angle of the IR beam of 45° recording 60 scans with a resolution of 4 cm⁻¹. The spectra were processed with OPUS (BrukerOptik GmbH, Ettlingen, Germany) and OMNIC (Nicolet Instrument, Madison, EEUU) software packages.

¹H- and ¹³C-Nuclear Magnetic Resonance (NMR). NMR spectra of the ECN and ECN+HHA mixtures were obtained in Bruker AC-400 spectrometer (Bruker, Rheinstetten, Germany) with 400 MHz magnet and dual probe ¹H/¹³C (5 mm). Experiments were carried out by using 30-40 mg of sample, and deuterated acetone or deuterated chloroform were used as solvents; TMS (trimethylsilane) was used as internal reference. The NMR spectra were processed with Mestrec 5.0 software (Mestrelab Research S.L., Santiago de Compostela, Spain).

Thin Layer Chromatography (TLC). The reaction of the ECN and the HHA was evidenced by TLC. The chromatographic silica gel plates used were DC-Fertigfolien Alugram Xtra SIL G/UV (Macherey-Nagel, Düren, Germany). Phosphomolibdic acid was used as TLC developer. The ECN

and ECN+HHA polymers were dissolved in acetone, and one drop of the HHA and the ECN+HHA mixture was placed at the bottom of the vertically placed chromatographic plate. The rising of the drops was monitored by using 1/1 (v/v %) ethyl acetate/hexane mixture as eluent.

Differential Scanning Calorimetry (DSC). The structure and the thermal stability of the ECN and ECN+HHA polymers were analyzed by DSC in DSC Q100 instrument (TA Instruments, New Castle, DE, USA). 5-10 mg of the sample were placed in an hermetic aluminum pan and heated between -50 and 150 °C under nitrogen atmosphere (flow rate: 50 ml min⁻¹) by using a heating rate of 10 °C min⁻¹, followed by cooling down from 150 to -50 °C at the same rate. The existence of a post-polymerization reaction in the ECN and the ECN+HHA polymers was evidenced from the first DSC heating run. Afterwards, a second heating run from -50 to 300 °C was also performed by using a heating rate of 10 °C min⁻¹, and the glass transition temperature (T_g) and the decomposition of the polymers were determined.

Thermal gravimetric analysis (TGA). The thermal stability of the ECN and ECN+HHA polymers was analyzed in TGA Q500 instrument (TA Instruments, New Castle, DE, USA). 5-10 mg of the sample were placed in platinum crucible under nitrogen atmosphere (flow rate: 100 ml min⁻¹) and they were heated from room temperature to 350 °C by using a heating rate of 10 °C min⁻¹.

Chromatography Gas Mass Spectrometry (CG-MS). Low-resolution electron impact (EI) mass spectra were obtained at 70 eV by using He as carrier phase in Agilent 5973 Network Mass Selective Detector spectrometer (Santa Clara, USA). The samples were introduced through a GC chromatograph Agilent 6890N equipped with HP-5MS column [(5%-Phenyl)-methylpolysiloxane; length 30 m; ID of 0.25 mm].

Single lap-shear test. The adhesion properties of the ECN and the ECN+HHA mixtures were obtained from single lap-shear tests of flexible PVC/ECN+HHA/flexible PVC joints (Figure 2). Flexible PVC pieces of 80 x 25 x 1 mm were used and the adhesive was applied in an area of 10 x 25 mm. Before joint formation, the flexible PVC test samples (provided by Giovanni Crespi, Elche, Spain) were wiped with methyl ethyl ketone (MEK, Jaber, Móstoles, Spain) for plasticizer removal, and they were allow to evaporate for 30 minutes under open air. Then, 10 µL of the adhesive was applied on one flexible PVC test sample and the other was immediately placed on

the top. The joint was pressed at 2 bars for 1 minute. The adhesion was measured immediately and one hour after joint formation in Instron 4411 universal testing machine (Instron, Buckinghamshire, UK) by using a pulling rate of 100 mm min^{-1} . Ten replicates were tested and averaged.

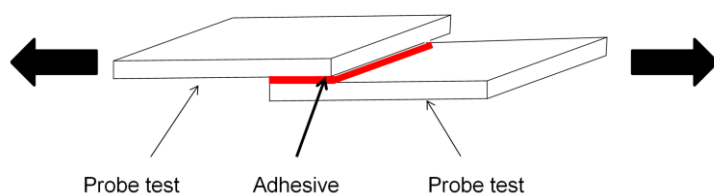


Figure 2. Test sample for measuring the single-lap shear strength of joints made with ECN and ECN+HHA mixtures.

3. RESULTS AND DISCUSSION

3.1. Adhesion of the ECN+HHA mixtures

The immediate and one hour after joint formation adhesive strengths of flexible PVC/adhesive/flexible PVC joints are given in Table 1. The adhesion of ECN increases when HHA is added, more noticeably for the immediate adhesive strength and by adding 10 v/v% of HHA. One hour after joint formation, the adhesive strength increases because of the polymerization of the ECN and the ECN+HHA mixtures is produced. A cohesive failure of the adhesive is observed in all joints. Since an increase in the adhesive strength in the joint made with ECN+10% HHA is observed, it seems that the addition of HHA favors the kinetics of ECN polymerization.

The properties of the ECN+HHA mixtures after long storage periods at $8 \text{ }^{\circ}\text{C}$ were monitored in order to mimic their storage conditions. Interestingly, after 90 days storage at $8 \text{ }^{\circ}\text{C}$, the visual aspect and the IR spectrum were similar to these of the freshly prepared ECN+HHA mixtures. On the other hand, after 192 days storage at $8 \text{ }^{\circ}\text{C}$ all ECN+HHA mixtures were liquid except ECN+10% HHA which showed a jelly aspect pointing to a polymerization produced during the

storage period. Therefore, the adhesion properties of the ECN+HHA mixtures stored during 90 days and the ECN+10% HHA mixture stored for 192 days were not measured.

Table 1. Immediate and one hour after joint formation adhesive strength of flexible PVC/adhesive/flexible PVC joints.

Mixture	Immediate adhesion		One hour adhesion	
	Shear strength (kPa)	Locus of failure	Shear strength (kPa)	Locus of failure
ECN	121 ± 28	CA*	208 ± 18	CA
ECN+5% HHA	130 ± 31	CA	259 ± 22	CA
ECN+10% HHA	268 ± 43	CA	267 ± 39	CA

*CA = Cohesive failure of the adhesive

Table 2. Adhesion strength obtained in the just-prepared and one hour after PVC/adhesive/flexible PVC joints formation. Influence of the storage time at 8 °C. A cohesive failure of the adhesive was obtained in all adhesive joints.

Mixture	Immediate (kPa)		One hour (kPa)	
	Initial	192 days	Initial	192 days
ECN	121 ± 28	70 ± 9	208 ± 18	87 ± 10
ECN+5% HHA	130 ± 31	56 ± 7	259 ± 22	66 ± 8

The adhesive strength values of the just-prepared and one hour after joint formation of flexible PVC/adhesive/flexible PVC joints made with ECN and ECN+5% HHA mixtures stored at 8 °C for 192 days are given in Table 2. After 192 days of storage at 8 °C, the joints made with ECN and ECN+5% HHA showed an important decrease in the adhesive strength, indicating that some polymerization was produced after this long period. All joints showed a cohesive failure in the adhesive.

3.2. Thermal stability of the ECN+HHA polymers

3.2.1. Polymers obtained from the just-prepared ECN and ECN+HHA mixtures

DSC thermograms corresponding to the first and second heating runs of the ECN+5% HHA polymer obtained from the just-prepared mixture is given as typical example in Figures 3a and 3b respectively. During the first DSC heating run, an endothermal post-polymerization is observed at 111 °C with an enthalpy of 19 J/g (Figure 3a). Therefore, under the experimental conditions used in this study, the polymerization of ECN is not complete. During the second DSC heating run, a completed polymerization was produced and the glass transition temperature and the decomposition of the fully polymerized ECN+5% HHA polymer can be evidenced (Figure 3b).

Table 3 show the values of some parameters obtained from the first and the second DSC heating runs of the ECN and ECN+HHA polymers obtained from the just-prepared mixtures. In the first heating run, the enthalpy of post-polymerization of the ECN is reduced by adding HHA, more noticeably by increasing the HHA content (Table 3), indicating that the addition of HHA favors the polymerization of the monomer. In the second heating run, the addition of HHA causes a decrease in the T_g value of the ECN polymer, more marked by increasing the amount of HHA in the mixture (Table 3), indicating higher flexibility. Furthermore, the decomposition enthalpy of the ECN polymer decreases by adding HHA, more noticeably by adding higher amounts of HHA, likely due to an intercalation of the HHA molecules between the ECN polymer chains.

Table 3. Some parameters obtained from the DSC thermograms of the ECN and ECN+HHA polymers obtained from the just-prepared mixtures.

Polymer	First heating run		Second heating run		
	$T_{\text{polym.}}$ (°C)	$\Delta H_{\text{polym.}}$ (J/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)
ECN	106	26	130	226	775
ECN+5% HHA	111	19	122	173-239	712
ECN+10% HHA	96	8	107	216-238	505

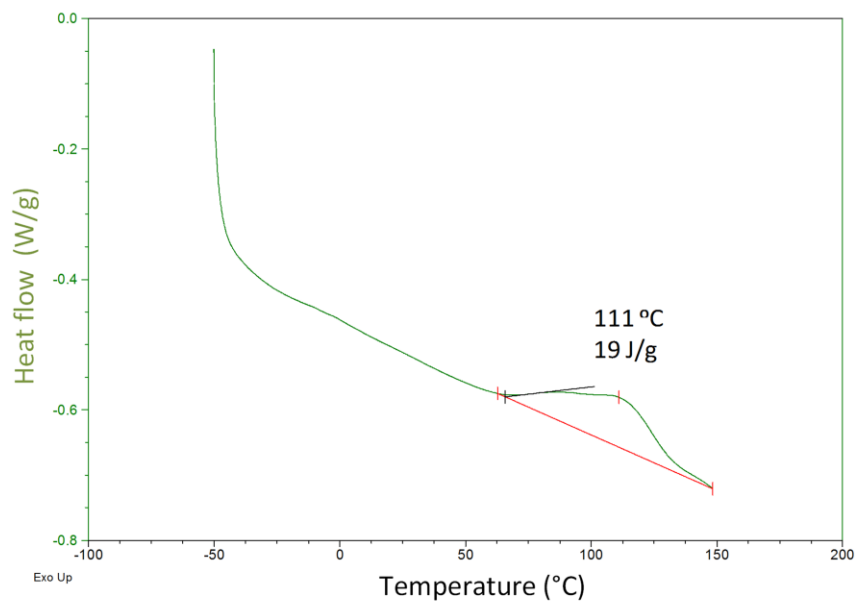


Figure 3a. DSC thermogram of the ECN+5%HHA polymer obtained from the just-prepared mixture. First heating run.

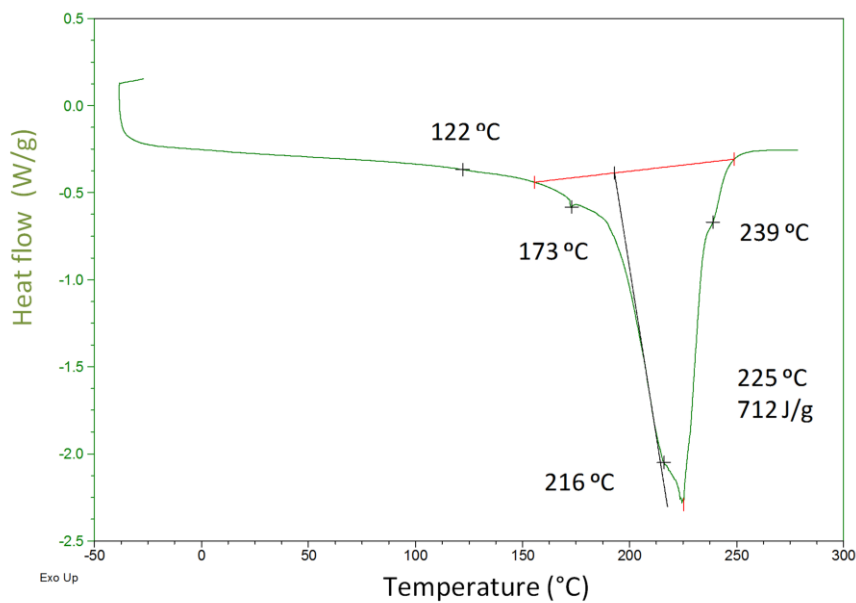


Figure 3b. DSC thermogram of the ECN+5% HHA polymer obtained from the just-prepared mixture. Second heating run.

The thermal stability of the polymers obtained from the just-prepared ECN and ECN+HHA mixtures was studied by TGA. According to Figure 4, between 125 and 200 °C, the highest is the HHA amount added to ECN, the lowest is the polymer stability. On the contrary, at temperatures above 225 °C, the thermal stability of the ECN+HHA polymers increases with respect to that of the ECN polymer. Therefore, at temperature below 200 °C the occluded HHA between the ECN polymeric chains is removed by heating, whereas the major thermal stability at higher temperature could be due to the formation of larger polymer chains of ECN produced by heating during TGA experiment.

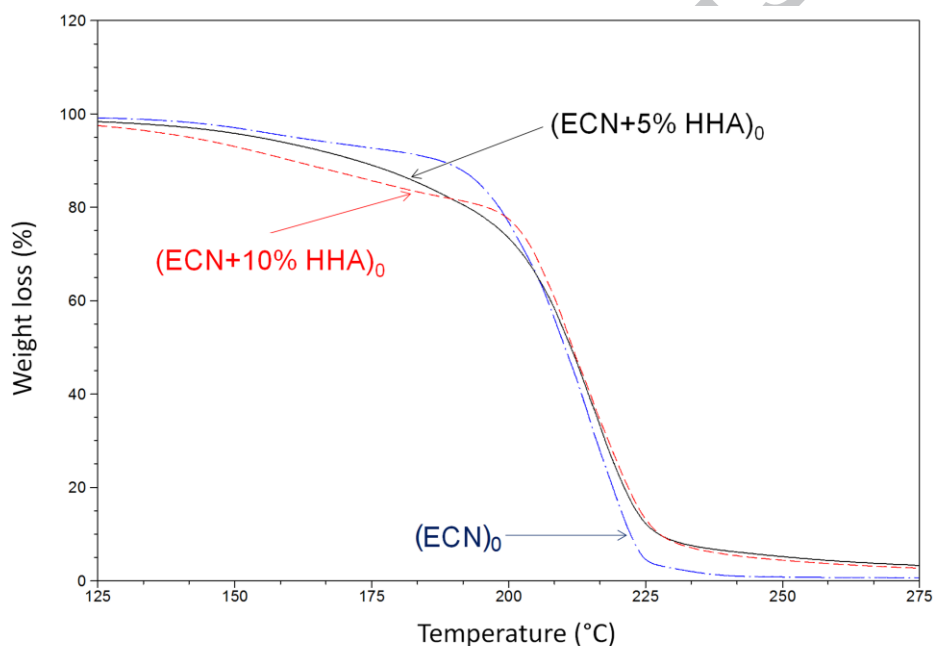


Figure 4. Variation of the weight as a function of the temperature for the ECN and ECN+HHA polymers. Just-prepared mixtures.

3.2.2. Polymers obtained from the ECN and ECN+HHA mixtures stored at 8 °C for 192 days

The thermal stability of the polymers obtained from the ECN+HHA mixtures stored at 8 °C during 192 days was also measured by using DSC and TGA. Table 4 shows the values of some parameters obtained from the first and second DSC heating runs. After 192 days, the

temperature at which post-polymerization of the ECN and the ECN+5% HHA polymers appears is displaced to higher values with respect to the same polymers obtained from the just-prepared mixture (from 111 to 144 °C in the ECN+5% HHA polymer, and from 96 to 131 °C in the ECN+10% HHA polymer). Similarly, the enthalpy of post-polymerization also increases in the polymer prepared from the mixture stored for 192 days (from 18 to 28 J/g in ECN+5% HHA polymer and from 8 to more than 189 J/g in ECN+10% HHA polymer). According to Table 4, the storage at 8 °C of the ECN+HHA mixtures for 192 days decreases significantly the T_g values of the polymers, more noticeably by increasing the HHA content in the mixture, and a decrease in the enthalpy of decomposition of the polymers is produced (from 712 to 656 J/g in the ECN+5% HHA polymer and from 505 to 207 J/g in the ECN+10% HHA polymer). These evidences indicate that a reaction between the ECN and the HHA is produced during the storage of the ECN+HHA mixtures.

Table 4. Some parameters obtained from the DSC thermograms of the ECN and ECN+HHA polymers obtained from the mixtures stored during 192 days.

Polymer	First heating run		Second heating run		
	$T_{\text{polym.}} (^{\circ}\text{C})$	$\Delta H_{\text{polym.}} (\text{J/g})$	$T_g (^{\circ}\text{C})$	$T_m (^{\circ}\text{C})$	$\Delta H_m (\text{J/g})$
(ECN) ₁₉₂	110	24	131	222	706
(ECN+5% HHA) ₁₉₂	100-144	28	112	224-242	656
(ECN+10% HHA) ₁₉₂	131	>189	100	196-275	207

Figures 5a) and 5b) compare the TGA thermograms of the ECN+5% HHA and ECN+10% HHA polymers obtained from the just-prepared and stored at 8 °C during 192 days mixtures, respectively. Below 150 °C, the thermogram of the (ECN+5% HHA)₁₉₂ polymer is similar to that of the one obtained from the just-prepared mixture. However, the thermal stability above 160 °C decreases noticeably in the (ECN+5% HHA)₁₉₂ polymer. On the other hand, according to Figure 5b, the (ECN+10% HHA)₁₉₂ polymer shows lower thermal stability at low temperature

(70-100 °C) than the $(\text{ECN}+5\% \text{HHA})_0$ polymer, probably due to the formation of oligomers and different species of low molecular weight during storage. The formation of these species could be a consequence of the nucleophilic reactivity of the HHA (this will be considered in the next section). For temperature above 100 °C, the thermal stability of the $(\text{ECN}+10\% \text{HHA})_{192}$ polymer is increased up to around 300 °C. The formation of longer polymer chains and the cross-linking of the ECN+10% HHA mixture during storage could justify the improved thermal stability.

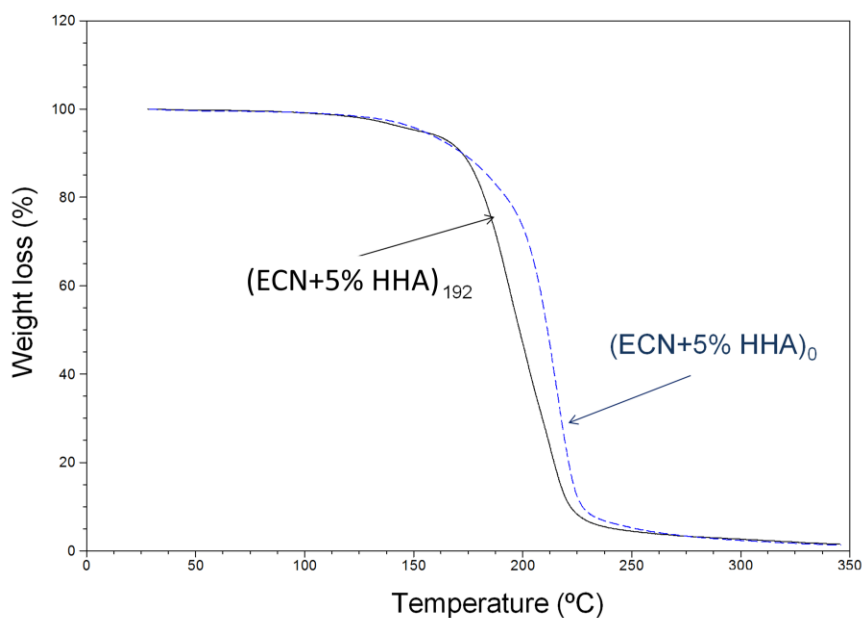


Figure 5a. Variation of the weight as a function of the temperature for the $(\text{ECN}+5\% \text{HHA})$ polymers obtained from the just-prepared and stored for 192 days mixtures.

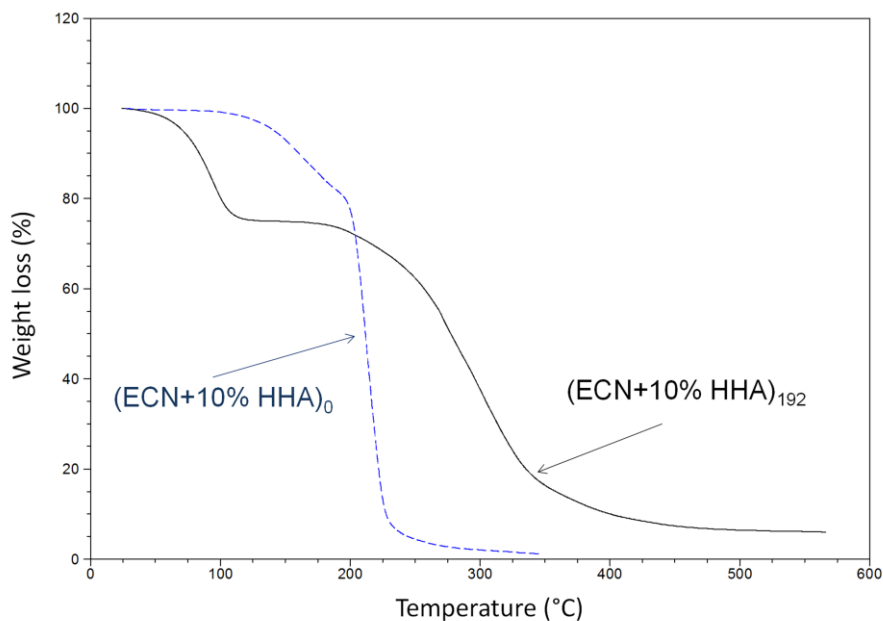


Figure 5b. Variation of the weight as a function of the temperature for the (ECN+10% HHA) polymers obtained from the just-prepared and stored for 192 days mixtures.

3.3. Reaction between ECN and HHA in the ECN+HHA mixtures

3.3.1. Reactivity of the just-prepared ECN+HHA mixtures and polymers

The electrophilic character of the C=C double bond of the HHA is lower than that for the C=C double bond in the ECN. [21] On the other hand, the amount of HHA is much lower than of ECN in the ECN+HHA mixtures. Therefore, the reactivity of the HHA is disfavored as electrophile, and the OH group of the HHA is a much poorer nucleophile than water. As a consequence, a reaction between the ECN and the HHA is not expected, irrespective of the amount of HHA added. The ATR-IR spectra of the ECN+HHA mixtures are given in Figure 6, and they do not show new absorption bands as compared to the ones of the ATR-IR spectra of the ECN and HHA, confirming the absence of reaction between them.

The thin liquid chromatogram (TLC) of the ECN+10% HHA polymer obtained from the just-prepared mixture is given in Figure 7. The TL chromatogram of the ECN+10% HHA polymer is

similar to that of the HHA, both having a retention factor (R_f) of zero. Thus, the HHA is totally or partially occluded into the polymer structure and no reaction between the ECN and the HHA is produced.

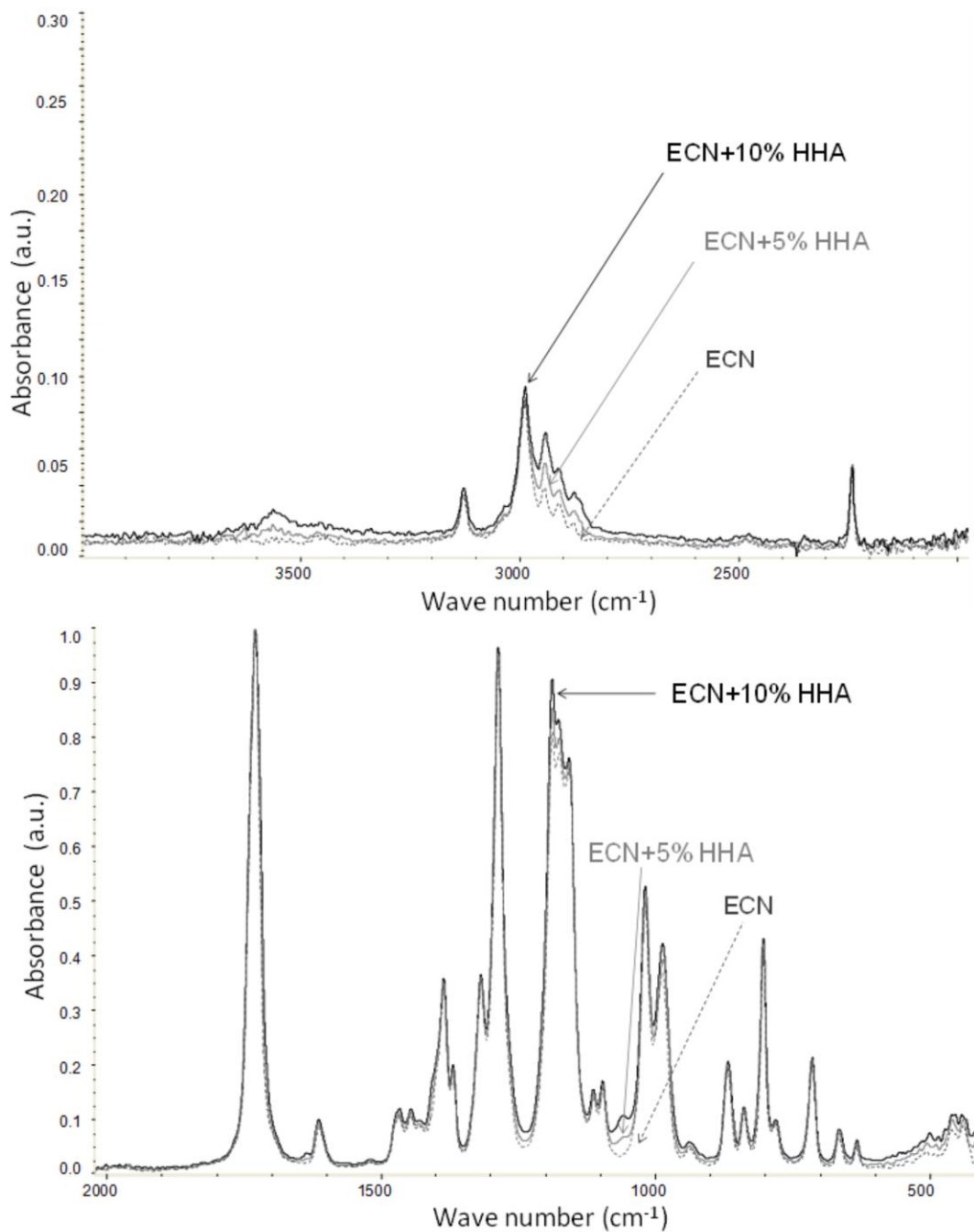


Figure 6. ATR-IR spectra of the just-prepared ECN and ECN+HHA mixtures.



Figure 7. TLC analysis (EtOAc/hexane: 1/1, v/v) for: **A** ECN+10%HHA polymer, and **B** HHA.

The occlusion of the HHA into the ECN+HHA polymers was also evidenced by NMR. The ^1H -NMR spectra of the HHA and ECN polymer (pECN) employing deuterated acetone as solvent are given in Figures 8a and 8b, respectively, and the ^1H -NMR spectrum (acetone- d_6) of the ECN+10% HHA polymer is shown in Figure 8c. All HHA absorption resonances are present in the ^1H -NMR spectrum of the ECN+10% HHA polymer, i.e. the olefinic (6.33 and 5.86 ppm) and CH_2O (3.51 ppm) protons. Since no new NMR signals could be distinguished, no reaction between the HHA

and the ECN is produced in the ECN+10% HHA polymer, and the HHA seems to be occluded into the polymer chains of the ECN polymer.

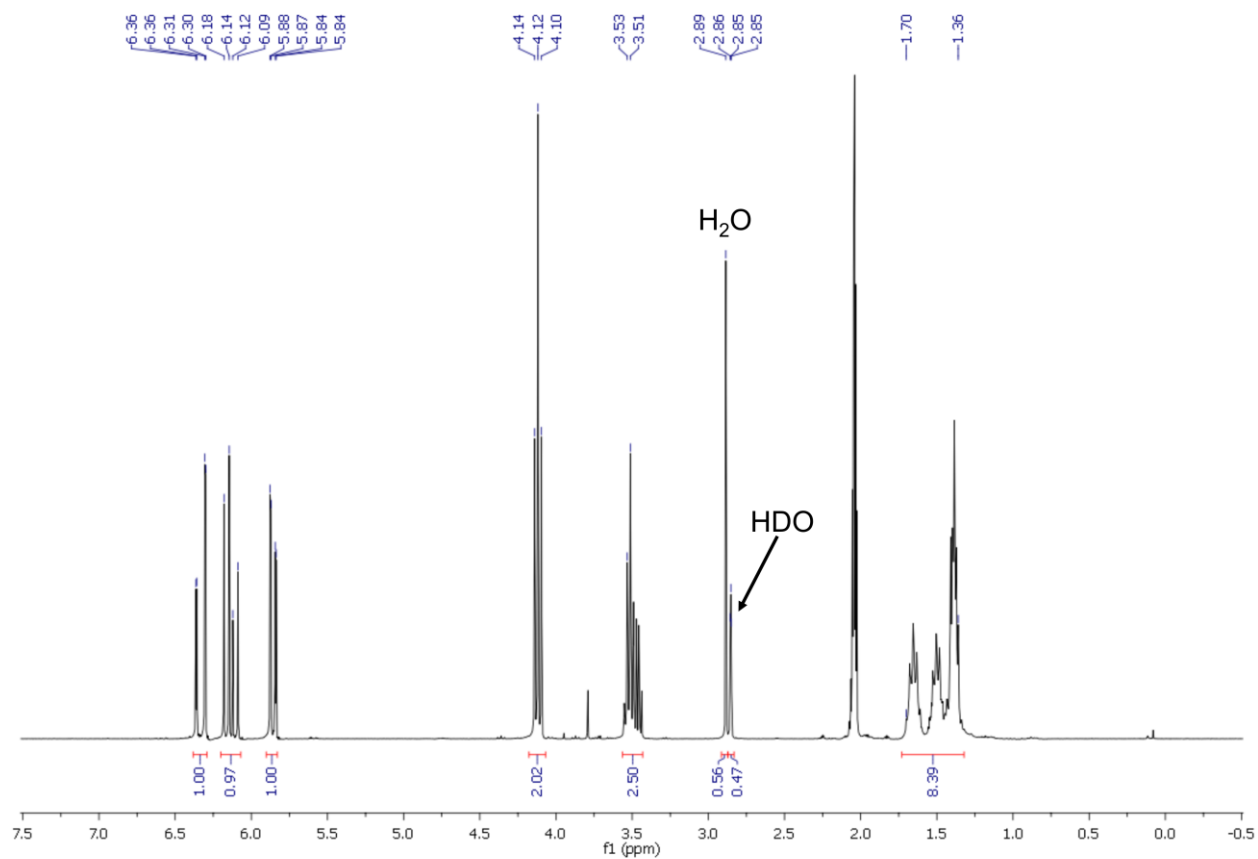


Figure 8a. ¹H-NMR spectrum (400 MHz, acetone-d₆) of HHA.

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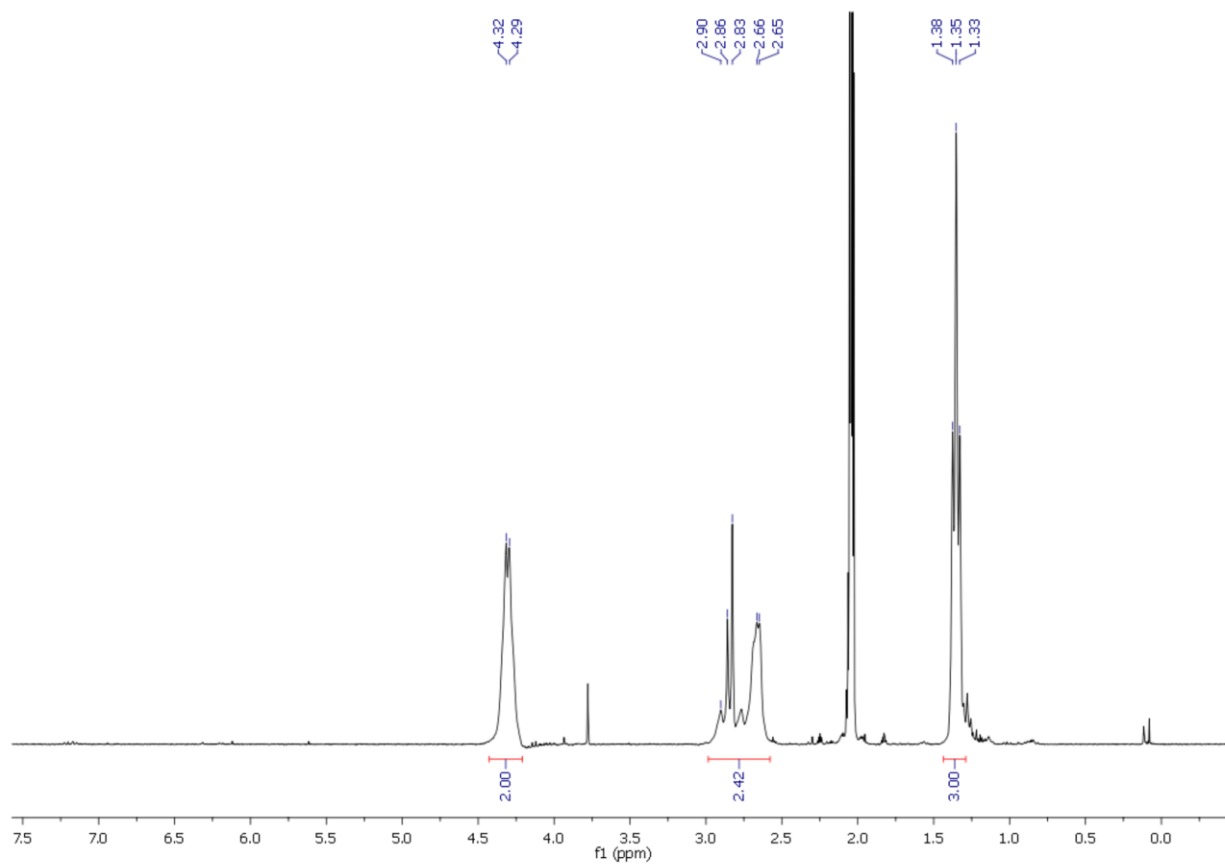


Figure 8b. $^1\text{H-NMR}$ spectrum (400 MHz, acetone- d_6) of the just prepared ECN polymer (72 hours after polymerization).

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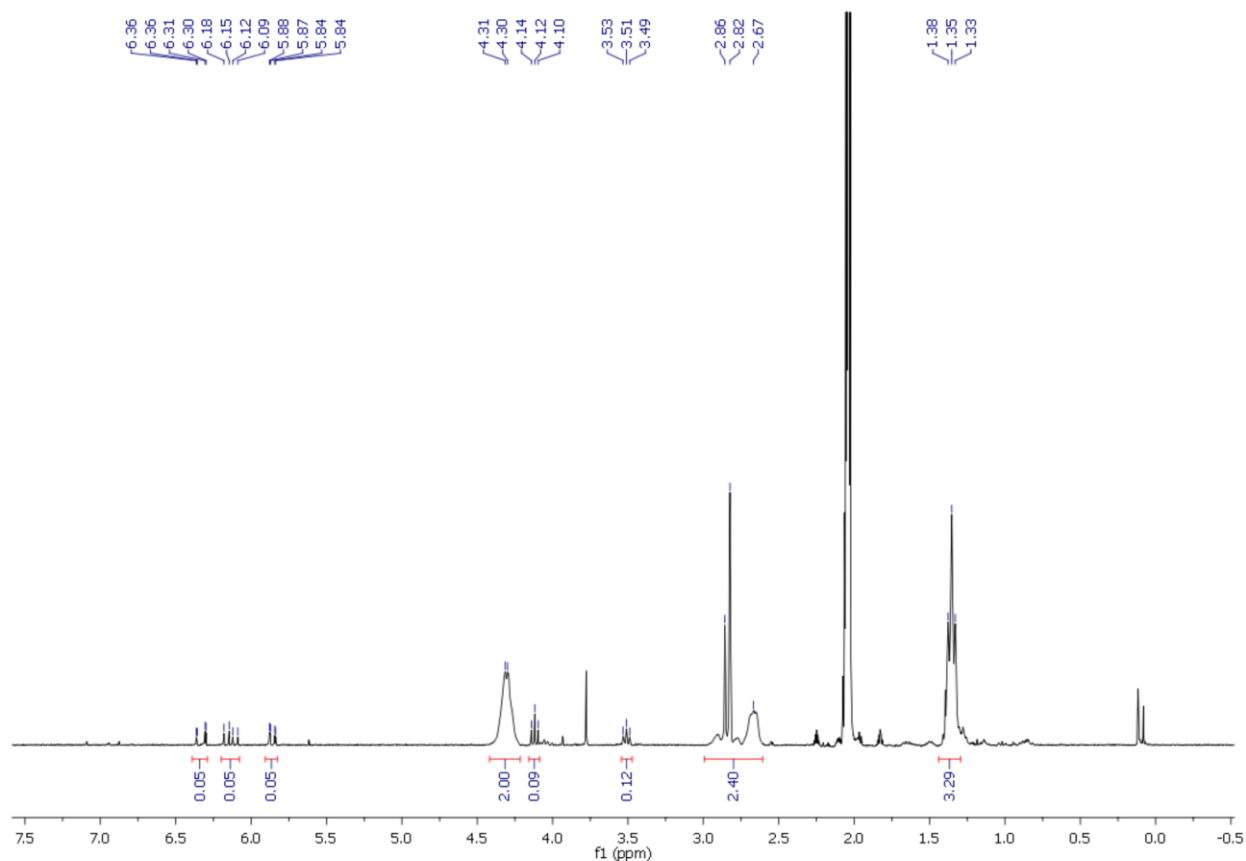


Figure 8c. $^1\text{H-NMR}$ spectrum (400 MHz, acetone- d_6) of the ECN+10%HHA polymer obtained from the just-prepared mixture (72 hours after polymerization).

The tacticity of the ECN+HHA polymers obtained from the just-prepared mixtures was analyzed by $^1\text{H-NMR}$ spectroscopy. Figure 9 shows the different possibilities for triads and tetrads in the ECN polymer. Denchev *et al.* [22] have established that the main tetrads in the ECN polymer corresponded to the rrr, rmr (both syndiotactic), and mmm (isotactic) structures. Based on these tacticity assignments, a comparison between the $^1\text{H-NMR}$ spectra of the ECN and the ECN+10% HHA polymers in the 2.6-3.0 ppm chemical shift region was carried out. No significant tacticity differences between the two polymers are obtained, being rrr, rmr, and mmm the major isomers observed (Figure 10). Consequently, the addition of HHA does not affect the tacticity of the ECN polymer, supporting the absence of reactivity between the HHA and the ECN in the ECN+HHA mixtures and polymers.

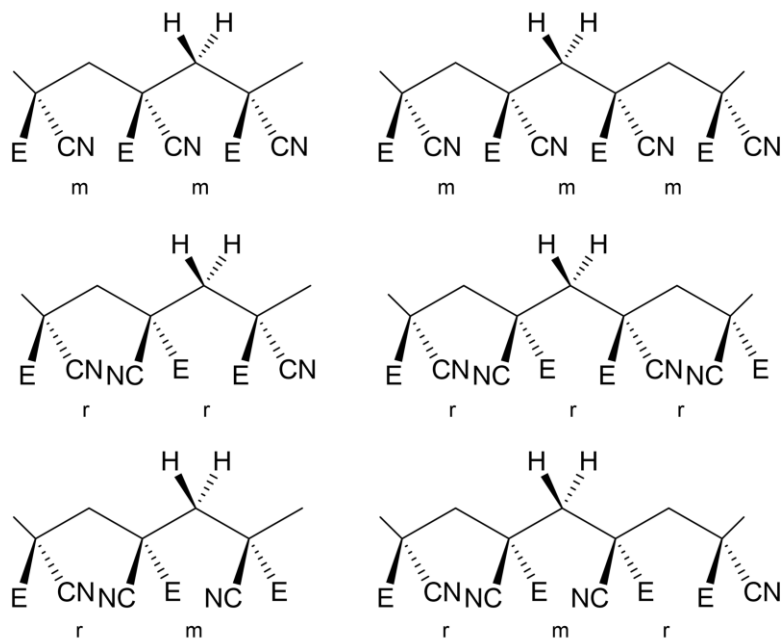


Figure 9. Triads mm, rr, and rm (left), and tetrads mmm, rrr, and rmr (right) of the ECN polymer. r = racemic isomer, m = meso form.

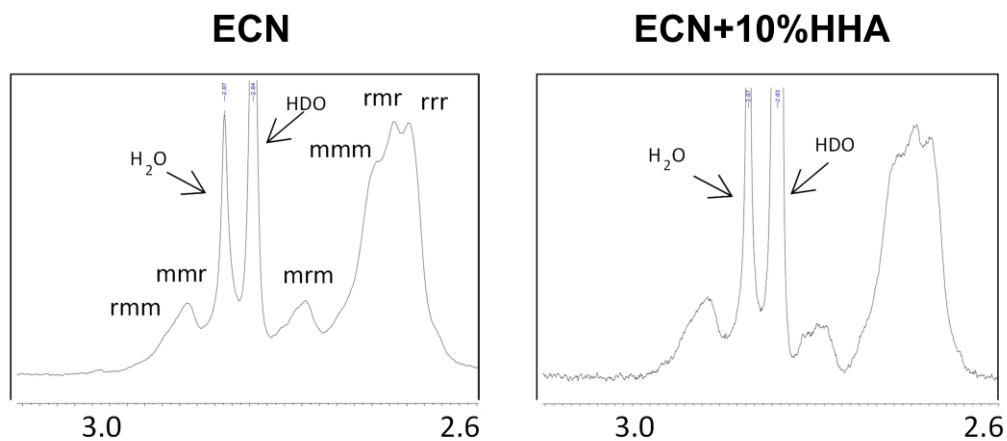


Figure 10. $^1\text{H-NMR}$ spectra (400 MHz, acetone- d_6 , 2.6-3.0 ppm) of the ECN and ECN+10%HHA polymers obtained from the just-prepared mixture.

3.3.2. Reactivity of the ECN+HHA mixtures and polymers stored at 8 °C for 90 and 192 days

The adhesion properties and the thermal stability of the ECN+HHA polymers changed with the time of storage suggesting a reaction between the ECN and the HHA. In this section, the ECN+HHA polymers prepared from the just-prepared mixtures will be identified as

(pECN+HHA)₀ and the ones prepared from the mixtures stored at 8 °C for 192 days mixtures will be identified as (pECN+HHA)₁₉₂.

Figure 11 shows the ATR-IR spectra of the just-prepared ECN+10% HHA mixture, and of the polymers obtained from the just-prepared (pECN+10% HHA)₀ and after 192 days storage at 8 °C (pECN+10% HHA)₁₉₂. The ATR-IR spectrum of the (pECN+10% HHA)₁₉₂ polymer does not show hydrogen-bonded O-H stretching band (ν O-H, 3600-3100 cm⁻¹), pointing to the involvement of the OH group of the HHA as reactive nucleophile in the polymerization of the ECN. Furthermore, the stretching band of the C-O-C group at 1250 cm⁻¹ decreases noticeably in the ATR-IR spectrum of the (pECN+10% HHA)₁₉₂ with respect to the (pECN+10% HHA)₀ polymer, confirming that a reaction between the ECN and the HHA is produced when the ECN+10% HHA mixture is stored for 192 days at 8 °C. On the other hand, the intensities of the C=C bands at 810 and 1636 cm⁻¹ are much lower in (pECN+10% HHA)₁₉₂ as compared to (pECN+10% HHA)₀, and the intensities are close to that of the C=C band of the HHA itself (1614 cm⁻¹). Thus, it seems that the double C=C bond in the HHA is not involved in the polymerization of the ECN.

Although the aliphatic alcohols are moderate nucleophiles,[21] after long storage periods they might react with good electrophiles such as carboxylic esters and Michael acceptors. Thus, two plausible reaction mechanisms between the HHA and the ECN can be considered (both ECN and oligomers produced during polymerization are considered as electrophiles).

- 1- The HHA may act as an initiator of the ECN polymerization by conjugate addition to the double C=C bond of ECN (Scheme 1, Eq. a). This adduct could be further involved in the polymerization creating new polymeric chains.
- 2- The HHA could suffer a transesterification with the ECN (Scheme 1, Eq. b), and, in fact, an easy transesterification between the HHA and the ethyl acetate at room temperature during the synthesis of HHA was observed. The transesterification between HHA and ECN does not initiate the polymerization, but creates a new monomer with higher molecular weight that would take part in the polymerization reaction. During the synthesis of HHA, the partial formation of 6-acetoxyhexyl acrylate – obtained by transesterification reaction of the ethyl acetate with HHA – was observed.

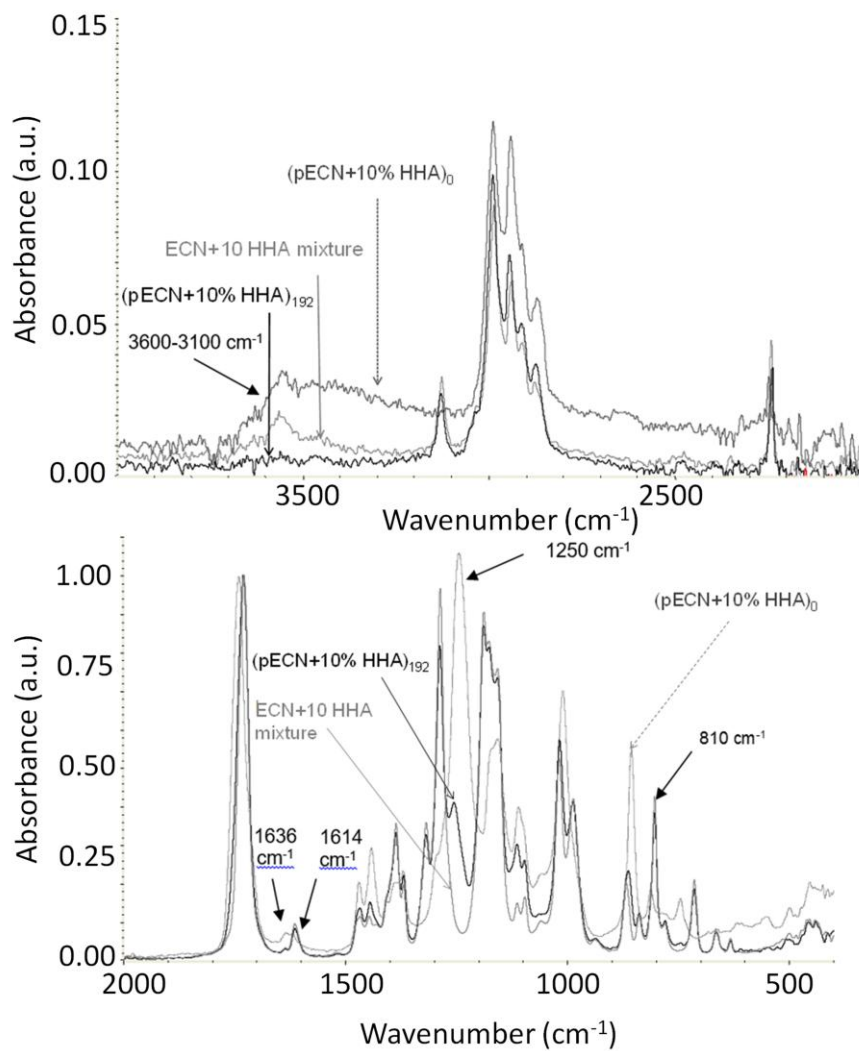
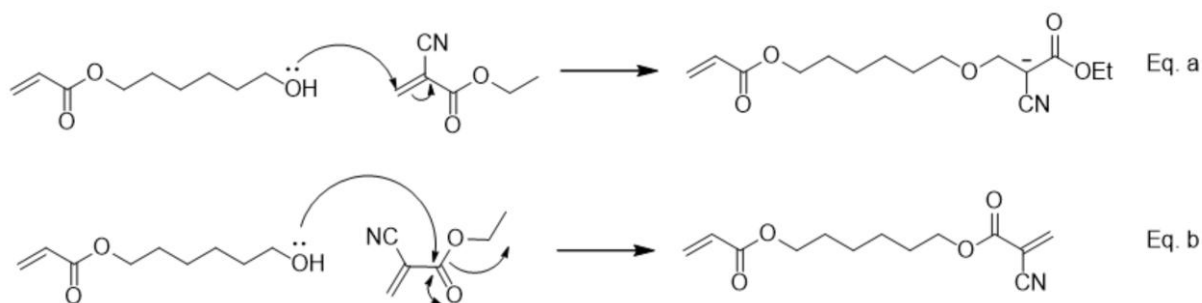


Figure 11. ATR-IR spectra of ECN+10% HHA polymers synthesized from just-prepared and after 192 days storage mixtures.



Scheme 1. Proposed mechanisms for the nucleophilic reactivity of HHA with ECN.

The mechanism of reaction of the ECN and the HHA was determined by TLC, GC-MS, and NMR. Figure 12 shows the TL chromatograms of (pECN+10% HHA)₁₉₂, (pECN+10% HHA)₀ and HHA. HHA is present in (pECN+10% HHA)₀ but not in (pECN+10% HHA)₁₉₂ pointing out to the existence of a covalent bond between the HHA to the ECN.

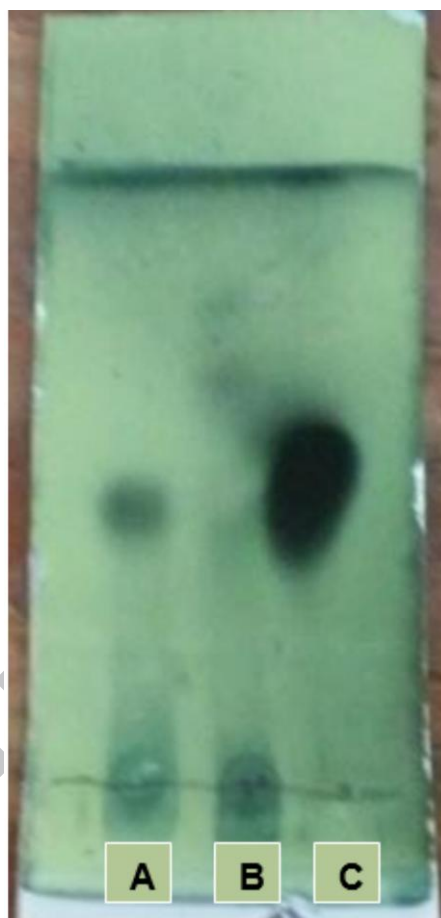


Figure 12. TLC analysis (EtOAc/hexane: 1/1, v/v) for: **A** (pECN+10% HHA)₀, **B** (pECN+10% HHA)₁₉₂, and **C** HHA.

The presence of free ECN in the (pECN+10%HHA)₁₉₂ polymer was evidenced by GC-MS. The ethyl acetate soluble fraction of the (pECN+10% HHA)₁₉₂ polymer was analyzed by GC-MS. According to Figure 13, the presence of ECN as main product (peak at a retention time of 4.05 min) together with very small amounts of ethyl 2-cyano-3-hydroxipropanoate (peak at a

retention time of 7.36 min) can be distinguished, the latter is obtained from the conjugate addition of water to ECN. Free HHA was not evidenced in the GC-MS chromatogram.

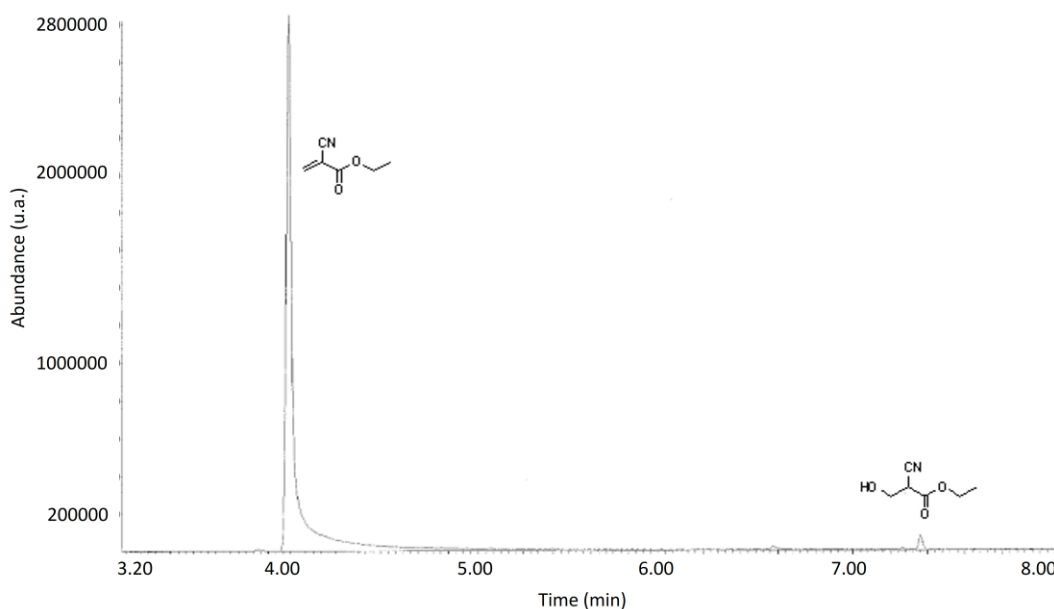


Figure 13. GC-MS chromatogram of the ethyl acetate soluble fraction of (pECN+10% HHA)₁₉₂ polymer.

Figure 14a shows the ¹H-NMR spectrum of (pECN+10% HHA)₁₉₂ that was normalized to the signals between 2.67 and 2.92 ppm of the two protons of the CH₂ produced during polymerization. The presence of non-reacted ECN is evidenced by the 2 singlets at 6.88 and 7.10 ppm, that correspond to the olefinic protons of the ECN monomer, and by the quartet of the CH₂O of the ECN at 4.32 ppm (*J* = 8 Hz) that is overlapped with the broad multiplet associated to the methylene of the ethoxy groups of the ECN polymer. On the other hand, the ¹H-NMR spectrum of (pECN+10% HHA)₁₉₂ also shows three olefinic absorption resonances at 6.39 (dd, *J* = 16.5, 1.5 Hz), 6.11 (dd, *J* = 16.5, 10.5 Hz), and 5.81 (dd, *J* = 10.5, 1.5 Hz) ppm, that do not correspond to the HHA but to the species formed by the nucleophilic reactions given in Scheme 1. Figure 14b shows the region of 3.40-4.50 ppm in the ¹H-NMR spectrum of (pECN+10% HHA)₁₉₂ for better analysis of the broad resonance between 4.20 and 4.40 ppm of the CH₂O group of the polymer. In Figure 14b the complex multiplets at 3.45-3.65, 3.80-4.00,

and 4.10-4.40 ppm can be distinguished, and some of them are not present in the $^1\text{H-NMR}$ spectrum of $(\text{pECN}+10\% \text{HHA})_0$. The appearance and shape of these sharp signals points to the existence of non-polymeric species indicating that during the polymerization new monomer and/or low-molecular weight oligomeric structures are formed. These results agree well with the lower thermal stability of $(\text{pECN}+10\% \text{HHA})_{192}$ evidenced in the TGA thermograms (Figure 5b).

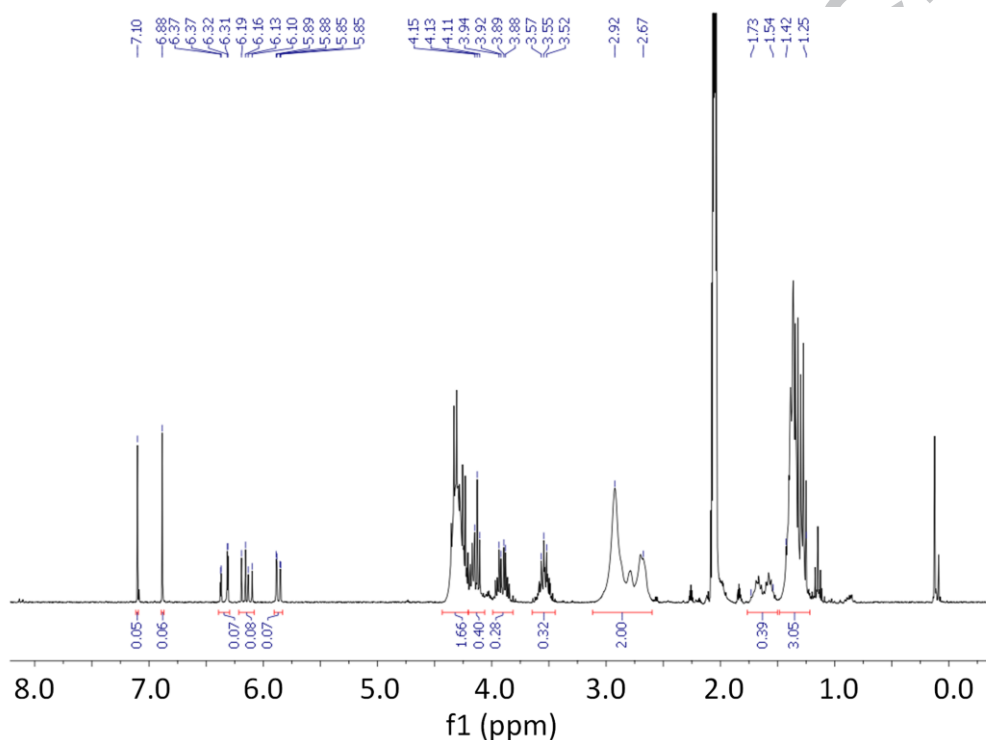


Figure 14a. $^1\text{H-NMR}$ spectrum (300 MHz, acetone- d_6) of $(\text{pECN}+10\% \text{HHA})_{192}$.

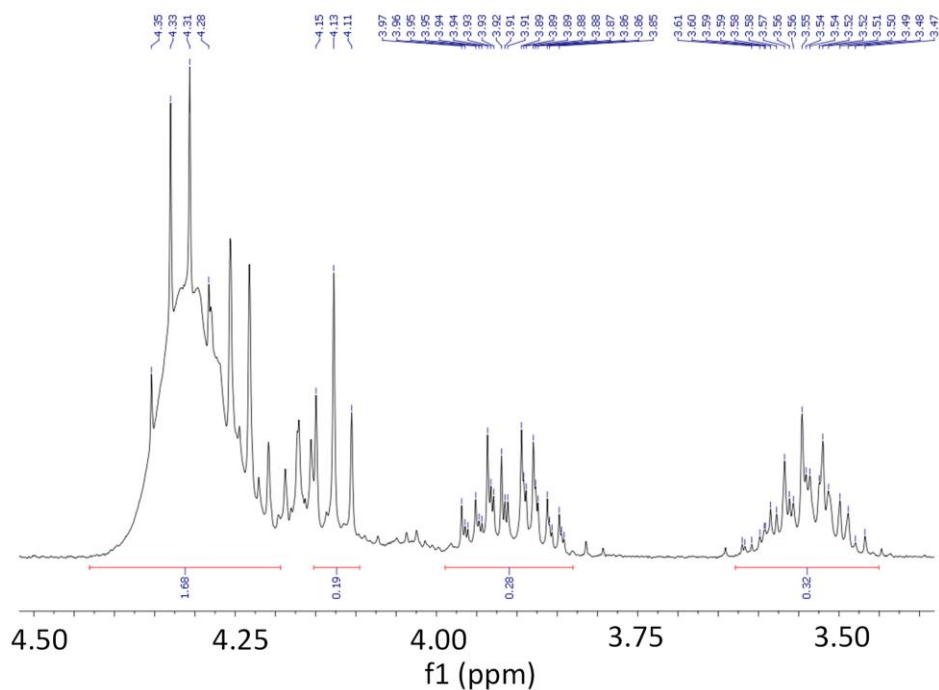


Figure 14b. $^1\text{H-NMR}$ spectrum (300 MHz, acetone- d_6 , 3.40-4.50 ppm) of (pECN+10% HHA) $_{192}$.

Considering the nucleophilic reactivity of the HHA towards ECN (or similar electrophilic entities with related structure), two main structural moieties can be formed in the ECN+HHA mixture stored at 8 °C for 192 days: one produced by reaction of the HHA via conjugate addition to ECN (**A**, Figure 15) and another formed by the transesterification of HHA with ECN (**B**, Figure 15).

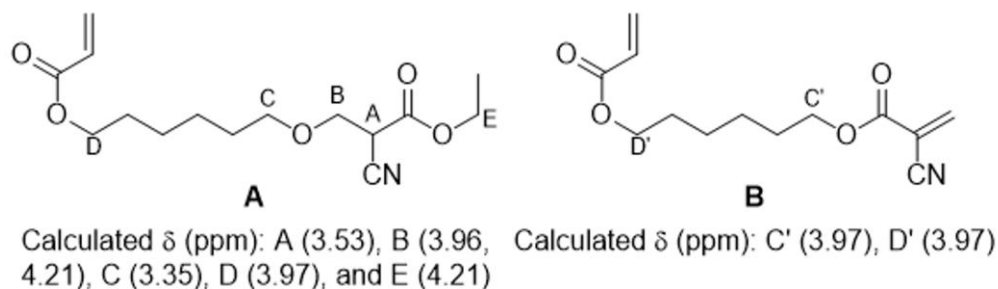


Figure 15. Chemical structure and calculated chemical shifts for compounds **A** and **B**.

The comparison of the $^1\text{H-NMR}$ spectra of $(\text{pECN}+10\% \text{HHA})_0$ (Figure 8c) and $(\text{pECN}+10\% \text{HHA})_{192}$ (Figure 14b) evidences clearly the existence of a new and complex signal between 3.80-4.00 ppm in $(\text{pECN}+10\% \text{HHA})_{192}$ that is better shown in Figure 16a. The chemical shift of that signal can be attributed to the diastereotopic protons B in the **A** structure of Figure 15 that are more shielded than the protons D but more deshielded than the protons C, according to previous study. The chemical shifts (ppm) for protons A (3.53), B (3.96, 4.21), C (3.35), D (3.97) and E (4.21) in structure A, were calculated by using ChemBioDraw Ultra v.14.0.0.117. Furthermore, the appearance of a complex doublet of doublets-type multiplicity [$^2J_{\text{BB}}$ (~9 Hz) and $^3J_{\text{AB}}$ (~6 Hz)] supports the presence of B-type protons of various structurally similar species. On the other hand, the multiplet between 3.4 and 3.65 ppm (Figure 16b) can be assigned to protons A and C of the **A** structure, and to protons C' of the **B** structure of Figure 17. Furthermore, the quartet at 4.32 ppm ($^3J = 9$ Hz) overlapped with a broad signal (4.20-4.45 ppm) (Figure 16c) can be attributed to the methylenic CH_2O groups of the residual ECN monomer and the polymeric structures respectively. Finally, the rest of the absorptions in the range 4.10-4.45 ppm would correspond to protons D, D', and E of the **A** and **B** structures. Therefore, the transesterification or Michael addition during storage of the ECN+10% HHA mixture seem to be produced.

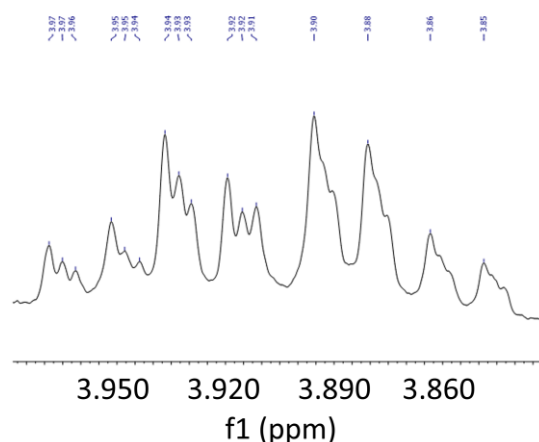


Figure 16a. $^1\text{H-NMR}$ spectrum (300 MHz, acetone- d_6 , 3.80-4.00 ppm) of $(\text{pECN}+10\% \text{HHA})_{192}$.

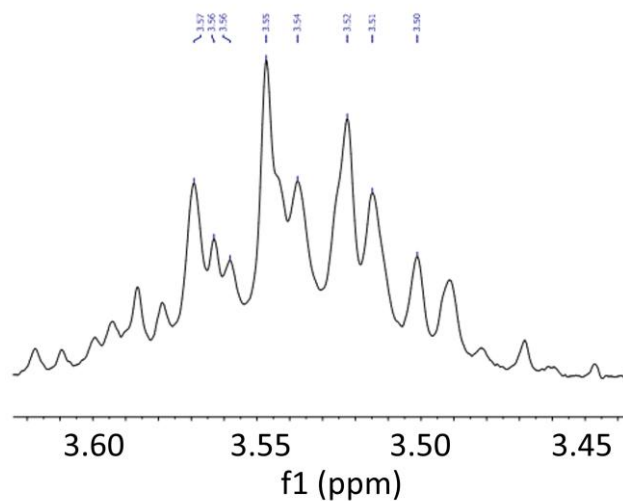


Figure 16b. $^1\text{H-NMR}$ spectrum (300 MHz, acetone- d_6 , 3.40-3.65 ppm) of $(\text{pECN}+10\% \text{HHA})_{192}$.

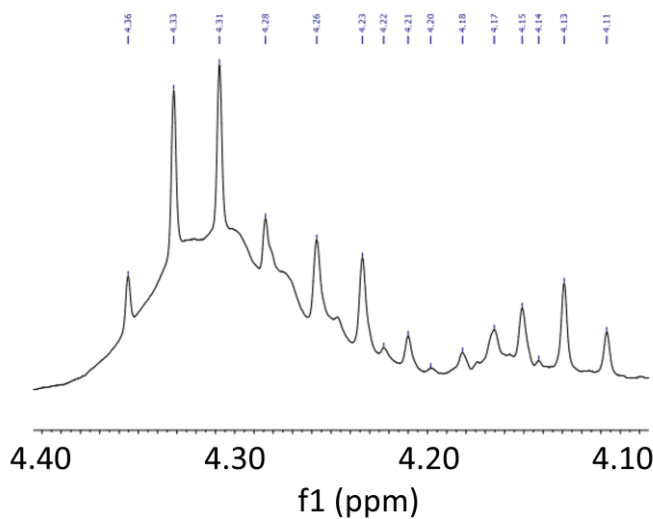


Figure 16c. $^1\text{H-NMR}$ spectrum (300 MHz, acetone- d_6 , 4.10-4.45 ppm) of $(\text{pECN}+10\% \text{HHA})_{192}$

The analysis of the $^1\text{H-NMR}$ spectrum of $(\text{pECN}+10\% \text{HHA})_{192}$ indicates that a large storage period of the ECN+10% HHA mixture favors the reactivity of the HHA and the ECN through transesterification and hetero-Michael reactions. However, the partial participation of the HHA as electrophile (as Michael acceptor) in the polymerization cannot be discarded by considering the relative integrals between the HHA-type olefinic protons (5.80-6.40 ppm) and those

attached to oxygen. The reactivity of the HHA with ECN could justify the observed changes in the physicochemical properties of the ECN+HHA polymers with the storage time. The higher thermal stability of these polymers with respect to the ECN polymer can be mostly explained by the formation of larger polymer chains slowly formed during longer storage times at 8 °C, and, to lesser extent, to the formation of copolymers between the ECN and the HHA or derivatives. Also, the transesterification of HHA with ECN will contribute to increase the thermal stability of the ECN+HHA polymers. On the other hand, the decrease of the T_g value can be ascribed to the existence of low molecular weight oligomers in the polymer formed by the transesterification reactions that produces species with a different alkyl substituent in the polymer chain that should decrease the interactions between the polymeric chains.

The tacticity of $(pECN+10\% HHA)_{192}$ also changes by increasing the storage time. The comparison of the signals between 2.6 and 3.0 ppm in the 1H -NMR spectra of $(pECN)_0$ and $(pECN+10\% HHA)_{192}$ (Figure 17) shows a strong reduction in the rrr, rmr, and mmm tetrads and an increase in the rrm, mmr, and mrm forms in $(pECN+10\% HHA)_{192}$. Because of the tetrads mmr and rrm are mainly isotactic and the tetrad mrm is mainly syndiotactic, the storage of the ECN+10% HHA mixture for 192 days produces a slow polymerization involving the HHA, and a polymer with isotactic structures is dominant.

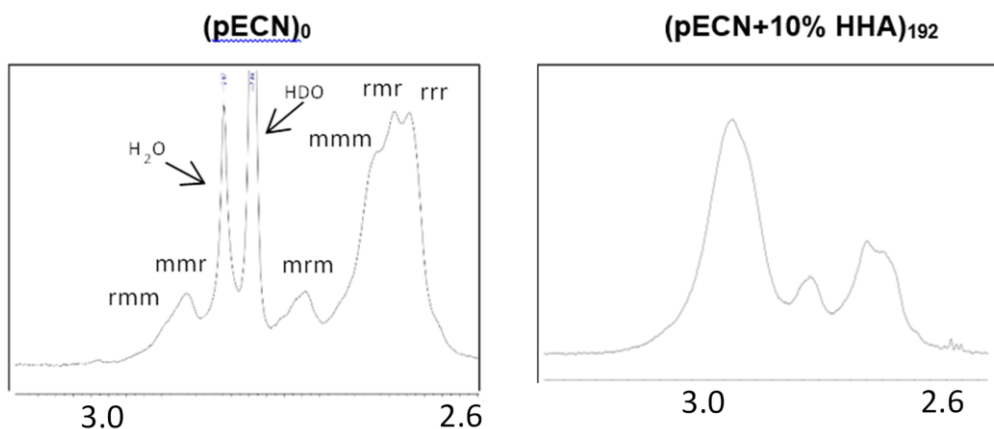


Figure 17. 1H -NMR spectra (400 MHz, acetone- d_6 , 2.60-3.00 ppm) of $(pECN)_0$ and $(pECN+10\% HHA)_{192}$.

Robello *et al.*[23] determined the tacticity of poly(ethylcyanoacrylates) by ^{13}C -NMR spectroscopy by analyzing the intensity and the chemical shift of the signals between 43-47 and 64-67 ppm which correspond to the polymeric triads and tetrads. Following Robello's assignments, the ^{13}C -NMR spectrum of (pECN+10% HHA)₁₉₂ (Figure 18) shows that the rmr and rrm tetrads are dominant, in agreement with the evidences shown by ^1H -NMR spectrum. Therefore, the polymerization of the ECN+10% HHA mixture stored for 192 days produces a polymer with different tacticity than in the ECN polymer.

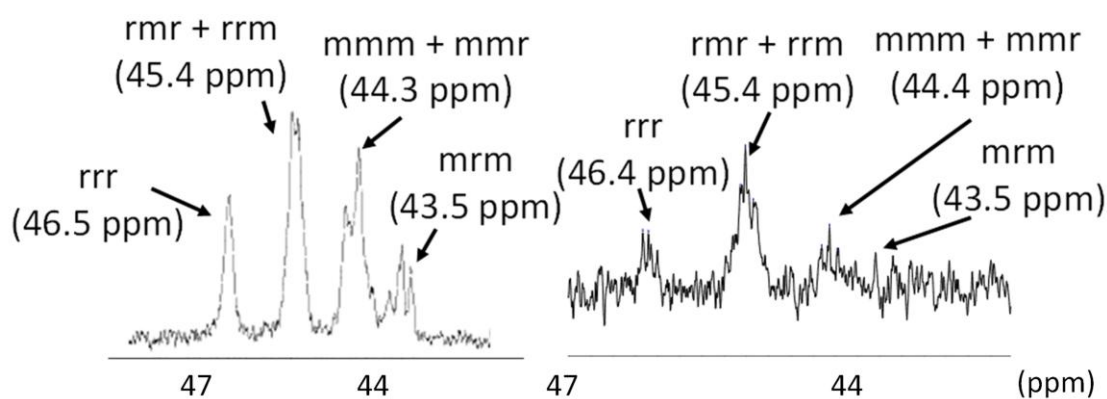


Figure 18. DEPT-135 spectra (75 MHz, acetone- d_6 , 43.0-47.0 ppm) of ECN polymer (left), and (pECN+10% HHA)₁₉₂ (right).

4. CONCLUSIONS

The addition of HHA to ECN produces important changes in the adhesion and thermal stability of poly(ethylcyanoacrylates). The immediate adhesion of ECN is improved by adding HHA, more markedly by increasing the amount of HHA; however, the final adhesion of ECN is reduced by adding HHA. On the other hand, the addition of HHA increases the flexibility of the ECN polymeric chain reducing the T_g value because of the occlusion of HHA molecules in the ECN polymer chains. Regardless HHA is added or not to ECN, the preferred polymer tacticity is syndiotactic. However, when increasing the storage time at 8 °C of the ECN+HHA mixtures an unexpected polymerization is detected affording isotactic polymeric species. According to our

studies, the effective shelf-life of the ECN+HHA mixtures is greater than 90 days but lower than 192 days. The reaction of HHA with ECN can be ascribed to slow transesterifications and/or Michael additions processes that led to the formation of low molecular weight oligomers and high molecular weight polymers, thus increasing the thermal stability.

Funding: This work was supported by the University of Alicante (VIGROB-173) and the Spanish Ministerio de Economía y Competitividad (CTQ2015-66624-P).

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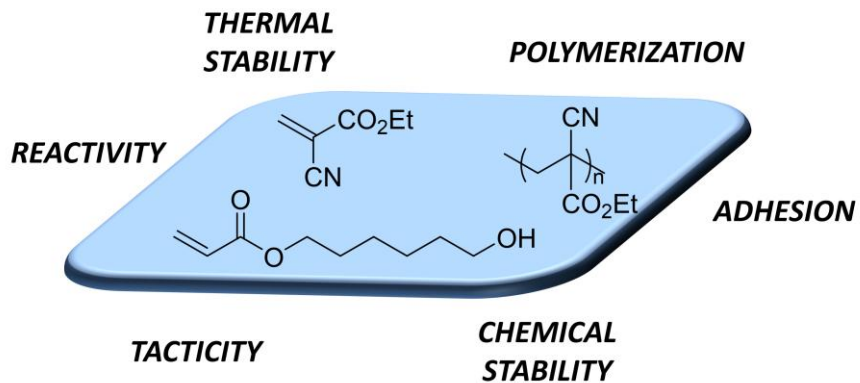
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Graphical abstract



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Highlights:

- The addition of HHA increases the immediate adhesion of ECN.
- HHA decreases the stiffness and improves the thermal stability of ECN.
- Copolymerization between HHA and ECN is produced after long periods of time.

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