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The isolation of a zwitterionic initiating species for ethyl cyanoacrylate (ECA) polymerization and the identification of the reaction products between 1°, 2°, and 3° amines with ECA

P. Klemarczyk*

Loctite Corporation, 1001 Trout Brook Crossing, Rocky Hill, CT 06067, USA

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Abstract

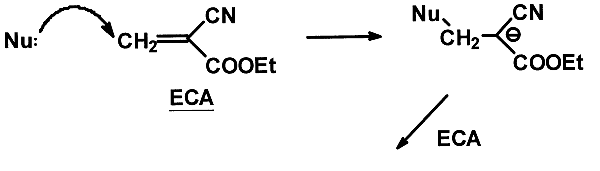
A study was conducted to investigate the differences in reactivity between ethyl cyanoacrylate (ECA) with phosphines and amines, which contain different alkyl substituents. It was found that when an equimolar amount of dimethylphenylphosphine and ECA react, a stable zwitterion is formed. This is the first time the proposed initiating species for alkyl cyanoacrylate polymerization has been sufficiently stable to be isolated and fully characterized spectroscopically. In contrast, triphenylphoshine reacts with ECA to form polymer, regardless of the molar ratio between the monomer and initiator.

The reactivity between primary, secondary, and tertiary amines and ECA also exhibit significant differences. Tertiary amines initiate rapid ECA polymerization with a strong exotherm to produce high molecular weight polymers. In contrast, the reaction of ECA with primary or secondary amines occurs at a much slower rate resulting in low molecular weight oligomers or polymers. After a ^{1}H NMR and IR spectroscopic study, it was demonstrated that intramolecular proton transfer occurs after the initial Michael-type addition of the primary or the secondary amine to the ECA double bond to form aminocyanopropionate esters. The differences in reactivity among the three classes of amines with ECA can now be attributed to the initial formation of aminocyanopropionate esters for primary and secondary amines and only polymer for tertiary amines.

Keywords: Ethyl cyanoacrylate; Amines; Phosphines

1. Introduction

Alkyl cyanoacrylate instant adhesives are utilized in a variety of applications because of their ability to very quickly bond a wide range of substrates under ambient conditions [1,2]. An anionic species or a Lewis base, which exist on most substrate surfaces, initiates the rapid polymerization of alkyl cyanoacrylate monomers and results in high molecular weight adhesive polymers. Eq. (1) provides the generally accepted polymerization mechanism with a Lewis base as the nucleophilic initiator (Nu:) and ethyl cyanoacrylate (ECA), the most widely used commercial alkyl cyanoacrylate monomer:



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The mechanism involves initiator addition across the alkyl cyanoacrylate double bond in a Michael-type addition to produce a zwitterion, which subsequently reacts with additional monomer to form the adhesive polymer [3–5]. The end groups of ECA homopolymers have been characterized to demonstrate that the zwitterion must have formed to initiate ECA polymerization [6,7], but the zwitterion has never been directly isolated and fully characterized [15].

Despite their extensive use in instant adhesive products, the chemical reactivity of alkyl cyanoacrylate monomers is still not completely understood. Both amines and phosphines are sufficiently nucleophilic to initiate alkyl cyanoacrylate polymerization [3–5]. Based on the similar values of their pK$_a$'s [8], all amines should be equally capable of initiating ECA polymerization, but significant differences have been observed. For example, the reactivity of primary, secondary, and tertiary amines with ECA are quite different. Tertiary amines rapidly initiate ECA polymerization with a strong exotherm to produce high molecular weight polymers [9,10]. In contrast, the polymerization of ECA with primary and secondary amines is much slower and molecular weights of the resulting polymers

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* Tel.: +1-860-571-5100; fax. +1-860-571-5464.

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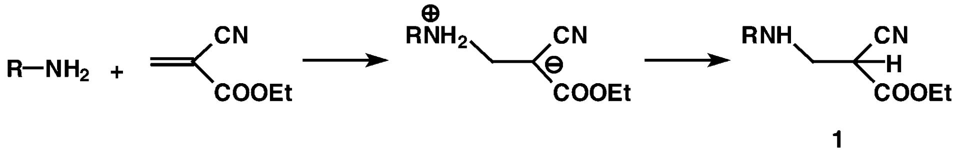
are decreased, relative to those polymers initiated by tertiary amines. Little or no exotherm is detected, even in bulk polymerizations [11].

Another example of these differences has been observed in certain adhesive applications. It has been shown that tertiary amines, which contain long alkyl chains, are effective primers for alkyl cyanoacrylate adhesives on polyolefin substrates, but primary and secondary amines, even if they contain long alkyl chains, are not [12].

Differences in reaction pathways, based on differences in alkyl substitution, might account for the differences in chemical reactivity between amines and ECA. An alternate reaction pathway, instead of polymerization, is available for primary or secondary amines after the formation of the zwitterion. Intramolecular proton transfer could be the preferred reaction to form an aminocyanopropionate ester, **1**, as shown in Eq. (2).



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This study was performed to analyze the products from the reaction of equimolar amounts of different amines and phosphines with ECA to determine if there is a correlation between the chemical structure of the phosphine or amine and its reactivity with ECA.

2. Experimental

2.1. Materials

The amines and phosphines were purchased from Aldrich and were used as received. Ethyl cyanoacrylate was obtained as a distilled monomer and used as received. THF was distilled from sodium/benzophenone immediately before use.

2.2. Instrumentation

Proton NMR spectra were obtained on a Varian Gemini 300 MHz NMR spectrometer. ^{31}P NMR spectra utilized H_3PO_4 as an external standard. IR analyses were done on an ATI Mattson genesis Series FT-IR. GPC analyses were performed with a Waters 600E Controller and pumps, PL gel 5μ mixed bed columns, a Waters 410 RI detector, and PSS Win GPC software for analysis.

2.3. Synthetic procedures

2.3.1. Preparation of the DMPP/ECA zwitterion, 4

Because of its severe stench, DMPP was handled as little as possible and in a fume hood. DMPP (0.22 g, 1.6 mmol) and ECA (0.2 g, 1.6 mmol) were dissolved separately in ca. 2 ml of $CDCl_3$. The ECA solution was added to the DMPP solution and an NMR spectra of this solution was obtained. The IR spectrum was obtained by evaporating a small amount of the NMR solution on a NaCl plate and allowing the solvent to evaporate.

2.3.2. Formation of methanesulfonate salt, 5

An equimolar amount of zwitterion, *4*, and MSA were dissolved separately in ca. 2 ml of $CDCl_3$. The zwitterion solution was added to the MSA solution. The ^{1}H and ^{31}P NMR spectra were then obtained, and the IR spectrum was taken by evaporating a small amount of the NMR solution on a NaCl plate and allowing the solvent to evaporate.

2.3.3. Ph_3P/ECA, ECA homopolymer

Triphenylphosphine (2.1 g, 8 mmol) was dissolved in 10 ml of THF. Ethyl cyanoacrylate (1.0 g, 8 mmol) was dissolved in 10 ml of THF. The ECA solution was added to the Ph_3P solution. After stirring for ca. 5 min, the reaction was quenched with 0.8 ml of con. HCl and added to 250 ml of MeOH acidified with 0.8 ml of con. HCl. The polymer precipitated, was collected by filtration, and was dried overnight at room temperature under vacuum. Yield = 0.91 g (91%).

2.3.4. Preparation of the amine/ECA adducts, 10, 11, and 12

Equimolar amounts of the amine and ECA (1.0 g, 8.0 mmol) were each dissolved in 10 ml of THF, and the ECA solution was added to the amine solution. After stirring for 5 min at room temperature, solvent was removed under reduced pressure, and the product was vacuum dried. An IR and a ^{1}H NMR spectrum were then obtained for each compound.

Table 1
Amines and their reaction products with ECA and ECA/MSA

Amine	Amine/ECA	Amine/ECA/MSA
Ethylamine, $EtNH_2$, **7**	$EtNH_2$/ECA, **10**	$EtNH_2$/ECA/MSA, **13**
Ethylamine, $EtNH_2$, **7**	$EtNH_2$/2 ECA, **11**	$EtNH_2$/2 ECA/MSA, **14**
Diethylamine, Et_2NH, **8**	Et_2NH/ECA, **12**	Et_2NH/ECA/MSA, **15**
Triethylamine, Et_3N, **9**	Polymer	

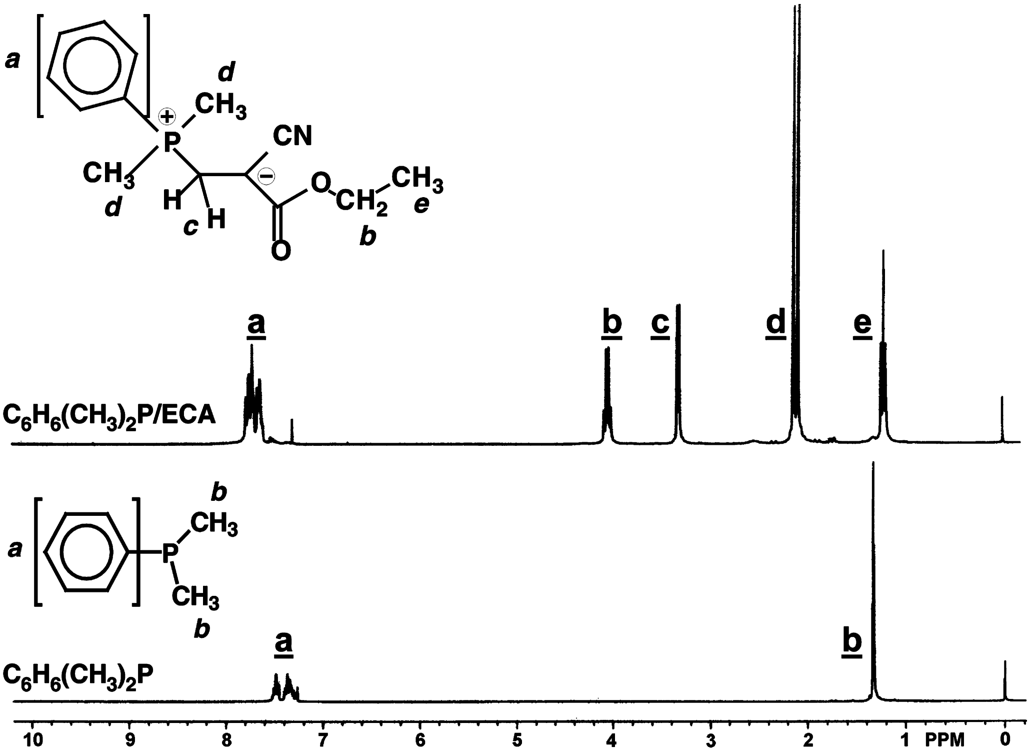


Fig. 1. ^{1}H NMR spectra of DMPP, **2**, and the DMPP/ECA zwitterion, **4**.

2.3.5. *Et_3N/ECA–ECA homopolymer*

The reaction of ethyl cyanoacrylate (1.0 g, 8 mmol) with triethylamine (0.81 g, 8 mmol) was performed in the same manner as for triphenylphosphine and ECA.

2.3.6. *Formation of amine/ECA methanesulfonate salts, **13**, **14**, and **15***

The amine/ECA adducts were synthesized as described earlier. An equimolar amount of the amine/ECA adduct and MSA were dissolved separately in ca. 2 ml of $CDCl_3$. The amine/ECA adduct solution was added to the MSA solution and a ^{1}H NMR spectrum was obtained. The IR spectrum was obtained by evaporating a small amount of the NMR solution on a NaCl plate and allowing the solvent to evaporate.

The amines that were employed in these experiments and the designation of their ECA and ECA/MSA reaction products are summarized in Table 1.

2.4. *GPC experiments*

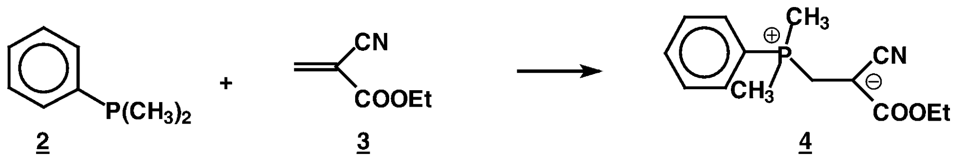
GPC analysis was conducted by dissolving 0.1 ml of the amine/ECA NMR solution in 10 ml of HPLC grade THF and filtering the GPC solution prior to GPC analysis. The GPC solvent was THF and the flow rate was 1.0 ml/min. Polystyrene standards were used for calibration.

3. Results and discussion

3.1. *Phosphines and ECA*

The reaction of triphenylphosphine (TPP) and ECA, even with an equimolar amount, yields only polymer and a large amount of unreacted TPP. The formation of the ECA homopolymer was confirmed by the very broad peaks at 4.2, 2.3, and 1.28 δ in the ^{1}H NMR spectrum for the ester $-CH_2$, the backbone $-CH_2$, and the ester $-CH_3$, respectively [14], and for a large quantity of unreacted TPP. It is well known that the molecular weight of an ECA homopolymer cannot be controlled by the molar ratio of ECA to initiator [9,10].

In contrast, the reaction product from an equimolar amount of dimethyl phenylphosphine (DMPP), **2**, and ECA, **3**, produces the stable DMPP/ECA zwitterion, **4**, as shown in Eq. (3),



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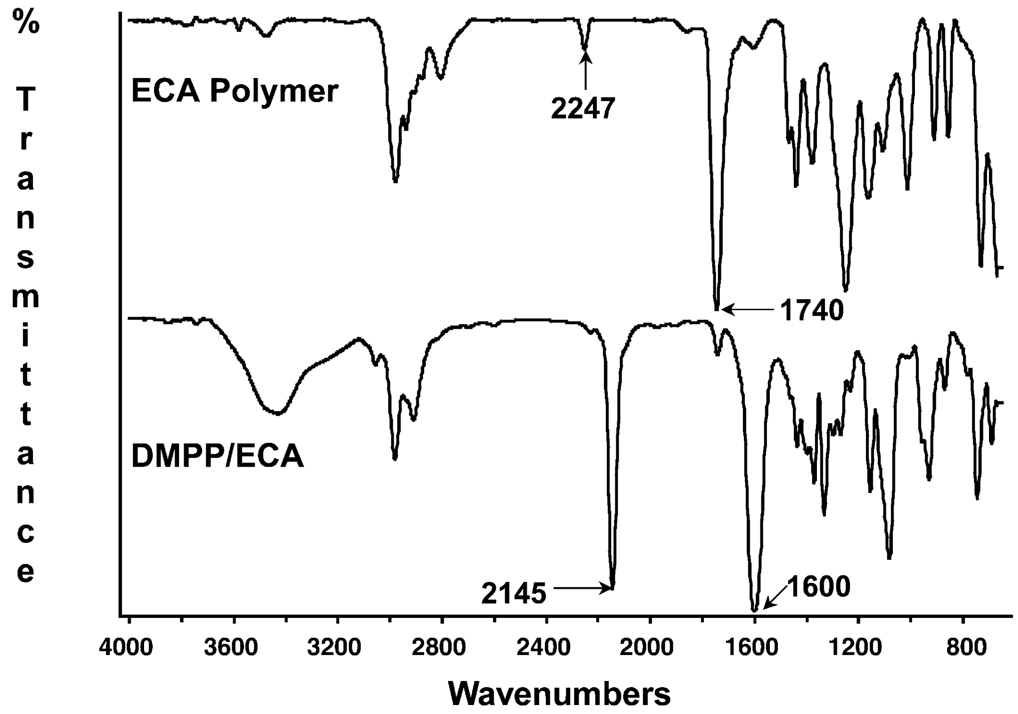

Fig. 2. IR spectrum of DMPP/ECA zwitterion, **4**, and ECA homopolymer.

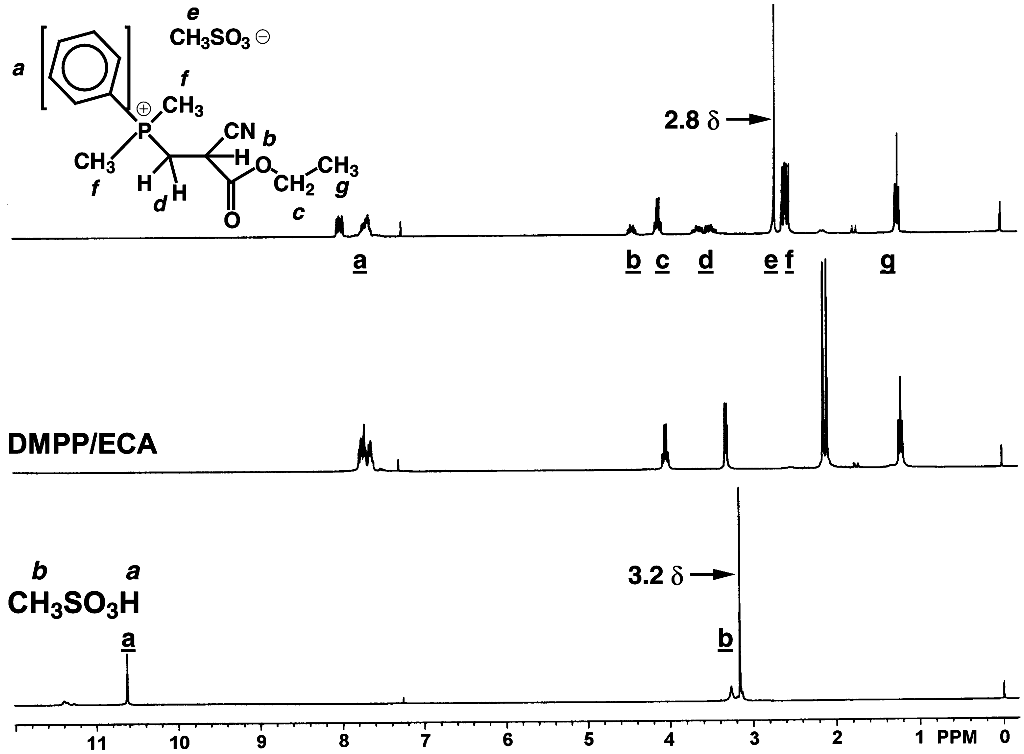

Fig. 3. ^{1}H NMR spectra of MSA, DMPP/ECA, **4**, and DMPP/ECA/MSA, **5**.

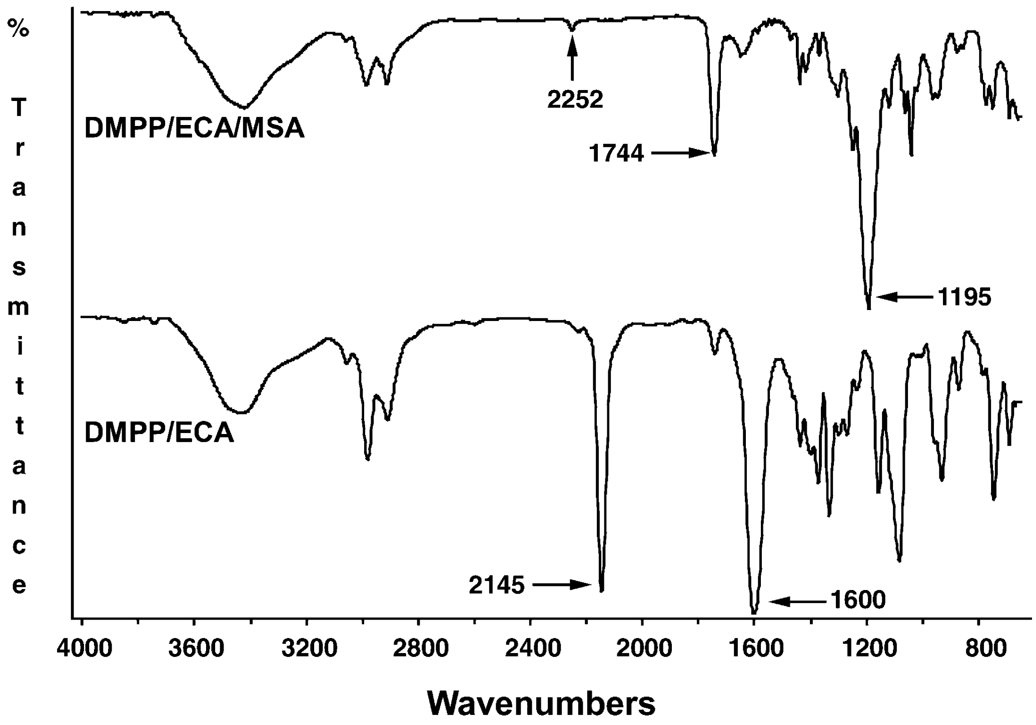

Fig. 4. IR spectrum for DMPP/ECA, **4**, and DMPP/ECA/MSA, **5**.

which can be isolated and characterized by ^1H NMR, ^{31}P NMR, and IR spectroscopy. This is the first time that the zwitterionic initiator species for alkyl cyanoacrylate polymers has actually been isolated and fully characterized [6,7]. The addition of an excess amount of ECA to zwitterion, **4**, produces the ECA homopolymer.

The ^1H NMR spectra of DMPP, **2**, and the DMPP/ECA zwitterion, **4**, are compared in Fig. 1. From analysis of the ^1H NMR spectra of zwitterion, it is clear that the starting materials have been consumed. For DMPP, the peaks for the aromatic protons and the CH_3 have shifted significantly, as seen in Fig. 1. For ECA, the peaks at 6.6 and 7.1 δ for the ECA $=CH_2$ protons are now absent, the peak for the OCH_2 protons shifted from 4.3 to 4.0 δ, and the peak for the CH_3 protons shifted form 1.4 to 1.2 δ. Also, ECA homopolymer has not formed because the proton peaks for **4** show distinct splitting and are not the broad, indistinct peaks for the ECA polymer. The peaks in the ^1H NMR spectrum correspond to those, which would be expected for the zwitterion.

Further evidence for the formation of the zwitterion can also be found in the IR spectrum of **4**, as shown in Fig. 2. The IR spectrum exhibits strong absorptions for the nitrile stretch and carbonyl stretch at 2145 and 1600 cm^{-1}, respectively, which is consistent for a molecule that contains a negative charge on the methine carbon. For a neutral molecule, which does not contain a negative charge, a weak nitrile absorption would be expected to appear at ca. 2250 cm^{-1} and a strong carbonyl absorption at ca. 1740 cm^{-1}. This is exactly what is observed for the ECA homopolymer, also shown in Fig. 2.

Additional data to confirm the existence of a zwitterion was demonstrated by its reaction with methanesulfonic acid (MSA). An equimolar amount of MSA was added to **4**, which produced a phosphonium methanesulfonate salt, **5**, as shown in Eq. (4).

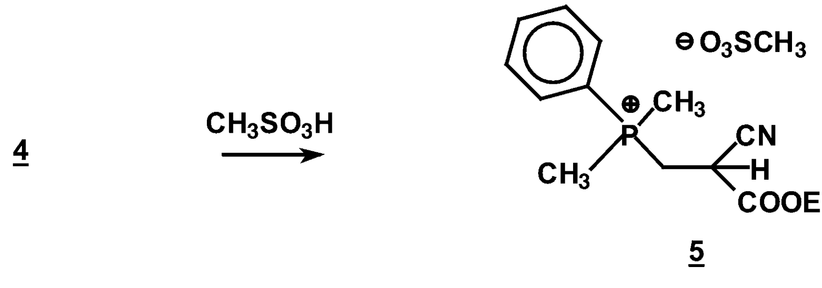

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Table 2
^{31}P Chemical shifts for **2**, **4**, and **5**

Compound	^{31}P Chemical shift
Dimethylphenyl Phosphine, **2**	36.4
4	24.8
5	22.3

Table 3
GPC molecular weight data

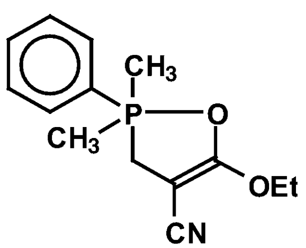
Amine/ECA Adduct	M_n	M_w	P.D.
Ethylamine/ECA	127	134	1.06
Ethylamine/2 ECA	148	157	1.07
Diethylamine/ECA	480	499	1.04
Triethylamine/ECA	23,200	123,000	5.28

The ^{1}H NMR spectrum of the phosphonium salt exhibited significant differences in the proton chemical shifts and coupling constants, compared to those of zwitterion, **4**, as seen in Fig. 3.

Major differences were also observed in the IR spectra of the zwitterion and its methanesulfonate salt, as seen in Fig. 4. The zwitterion displays an intense nitrile absorption at 2145 cm^{-1} and a carbonyl absorption at 1600 cm^{-1}, but the methanesulfonate salt, **5**, possesses a very weak nitrile absorption at 2252 cm^{-1} and a moderate carbonyl absorption at 1744 cm^{-1}. The latter two absorptions are located in the expected regions and with the expected intensities for a neutral nitrile and an ester carbonyl.

Finally, ^{31}P NMR spectra were obtained for dimethylphenyl phosphine, **2**, zwitterion **4**, and its methanesulfonate salt, **5**. The ^{31}P NMR chemical shifts for phosphorous atom in the three compounds are listed in Table 2.

The ^{31}P chemical shift of 24.8 ppm for **4** is final confirmation of its tetracoordinate, zwitterionic structure, because it is well known that such species have a chemical shift in the 10–50 ppm region of the NMR spectrum [13]. This data also eliminates the possibility that a pentacoordinate, neutral species, **6**, could be the correct structure for **4**. The ^{31}P chemical shift for **6** would occur in the −50 to −80 ppm region of the NMR spectrum [13]. In addition, the cationic methanesulfonate salt, **5**, possesses a very similar chemical shift to **4**, which is an indication of a very similar structure.



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From these experiments, it is clear that the nature of the substituents on the phosphorous nucleophile can determine the nature of the reaction products of that particular nucleophile with ECA.

3.2. Amines and ECA

To examine the differences in the reactivity between 1°, 2°, and 3° amines with ECA, the reaction products from an equimolar amount of ECA with $EtNH_2$ (**7**) Et_2NH (**8**) and Et_3N (**9**) were isolated. The products were characterized by GPC, ^{1}H NMR and IR analysis. Ethylamine (**7**) was treated with one and two molar equivalents of ECA to determine if both protons could be transferred to two moles of ECA.

3.2.1. GPC analysis

GPC analysis was performed on all of these reaction products. Table 3 lists the molecular weight data obtained from the GPC analyses for reaction products of $EtNH_2$/ECA, **10**, $EtNH_2$/2 ECA, **11**, Et_2NH/ECA, **12**, and the ECA homopolymer from Et_3N/ECA.

The GPC analysis clearly demonstrates that high molecular weight ECA homopolymer forms only with a tertiary amine as the initiator, even with equimolar amounts of ECA and amine. The much lower molecular weight Michael-type addition adduct is isolated if an equimolar amount of a primary or secondary amine is added to ECA.

3.2.2. ^{1}H NMR analysis

The only reaction products from the addition of an equimolar amount of Et_3N to ECA are the ECA homopolymer and a large amount of unreacted triethylamine. ^{1}H NMR analysis revealed the broad peaks for the ECA homopolymer at 4.2, 2.3, and 1.28 δ, and large amount of unreacted Et_3N.

In contrast, the ^{1}H NMR spectrum for the $EtNH_2$/ECA adduct, **10**, exhibits a very different type of spectrum. The peaks are quite sharp with extensive coupling and there is little or no evidence for the presence of polymer or unreacted $EtNH_2$, as shown in Fig. 5.

The sharp peaks show definite splitting with appropriate chemical shifts for the $EtNH_2$/ECA Michael-type addition adduct, **10**, without the peak broadening that would be expected for a polymer. The integration area for the ester $-CH_3$ triplet at 1.4 δ is the same area for the amine $-CH_3$ triplet at 1.2 δ. However, the splitting patterns for the other proton peaks are much more complex than would be expected for the simple aminocyanopropionate ester. A doublet at ca 2.5 δ, a triplet at ca 3.5 δ, and a quartet at ca 3–4 δ would be expected to appear in the 2.5–4.0 δ region, instead of the actual multiple peaks. Some complexity might be expected because of the presence of diasteromers, but the splitting is more extensive than can be explained simply by the presence of diasteromers.

One mole of $EtNH_2$ was treated with two moles of ECA to determine if the initial Michael addition adduct would also

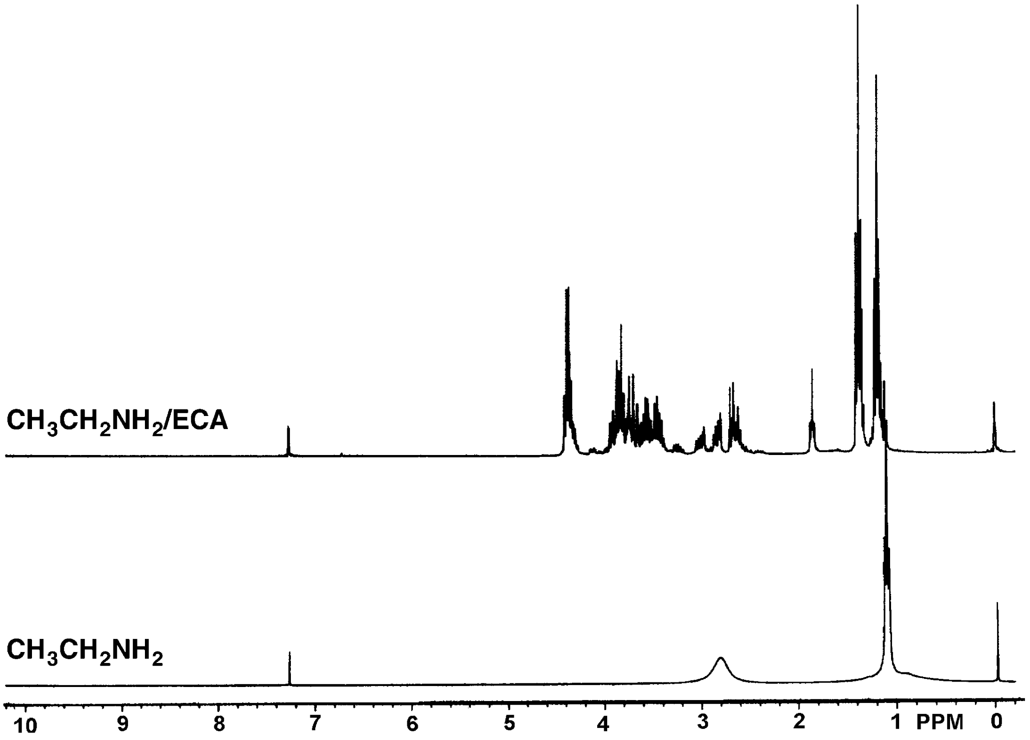
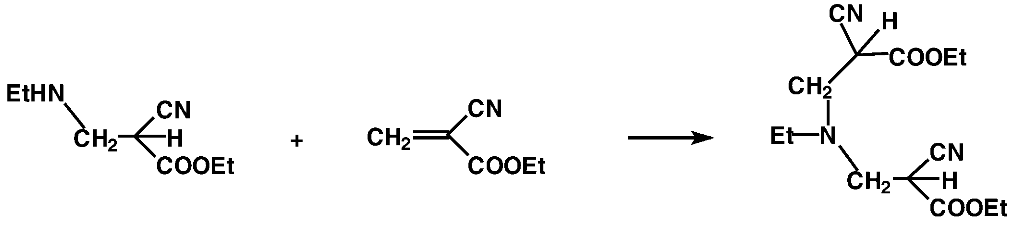


Fig. 5. ^{1}H NMR spectra of $EtNH_2$, **7**, and $EtNH_2$/ECA, **10**.

react with a second mole of ECA, to produce the bis-Michael-type addition adduct, as shown in Eq. (5):



10 **11** (5)

The ^{1}H NMR analysis for the $EtNH_2$/2 ECA adduct, **11**, revealed disinct peaks with complex splitting, as was seen for the $EtNH_2$/ECA adduct, **10**. The chemical shifts for the peaks of the various protons are in the same region as those for **10**, but are more intense in the 2.5–4.0 δ region and for the ester $-CH_3$, which would be consistent with the addition of a second mole of ECA.

From the GPC and ^{1}H NMR data, it is clear that one mole of $EtNH_2$ can react with either one or two moles of ECA.

The ^{1}H NMR spectrum for Et_2NH/ECA, **12**, exhibited a similar complex peak splitting pattern, as was observed for **10** and **11**, with the appropriate increases in the integration for the additional ethyl group.

The ^{1}H NMR does confirm the formation of aminocyanopropionate esters instead of ECA homopolymer in the reaction between ECA with primary and secondary amines, but the complexity of the spectra can be only partly explained by the existence of diastereomers. Other factors must also exist to create the multiplicity of peaks which are observed in the ^{1}H NMR spectra. The exact structure or structures for the amine/ECA Michael-type addition adducts was unclear based on the NMR data alone.

3.2.3. IR analysis

A compehensive IR study was then conducted to try to elucidate further the structures of the ECA/amine adducts.

The IR spectra for $EtNH_2$/ECA, **10**, and the ECA polymer from Et_3N/ECA are provided in Fig. 6. The NH stretch absorptions at ca. 3400–3500 cm^{-1} are

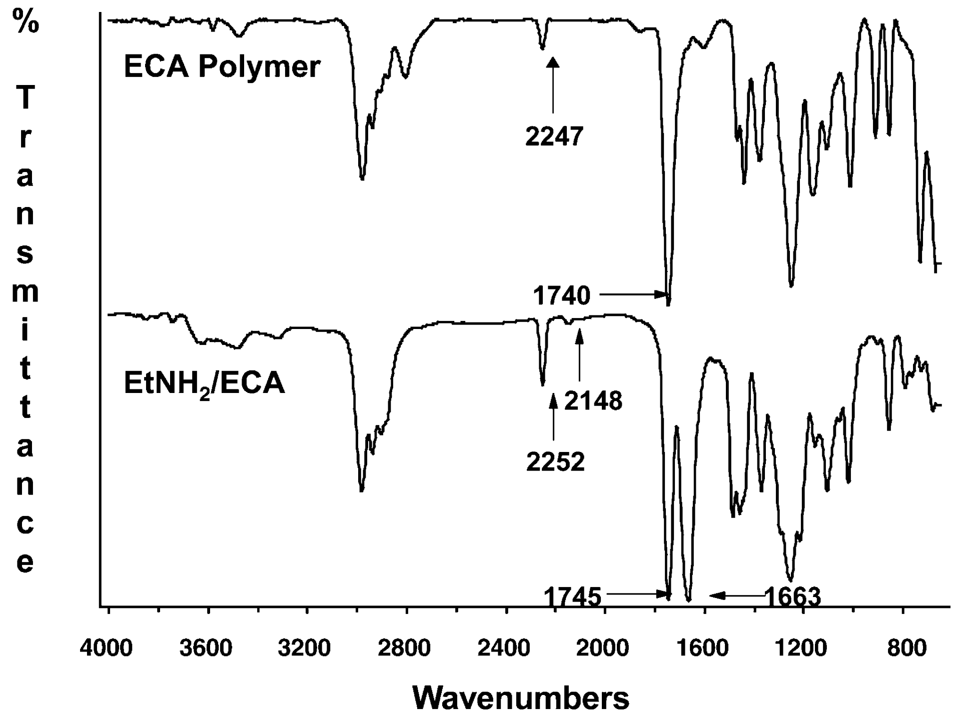


Fig. 6. IR spectra of $EtNH_2$/ECA, **10**, and ECA homopolymer from Et_3N/ECA.

weak, but still present, an indication that only one NH proton has reacted with ECA. There are two absorptions for the carbonyl stretch at 1745 and 1663 cm^{-1}, which is unlike that for the ECA homopolymer carbonyl absorption at 1740 cm^{-1}. A moderate absorption and a weak absorption are present for the nitrile stretches at 2252 and 2148 cm^{-1}, respectively.

The IR spectra for the $EtNH_2$/2 ECA adduct, **11**, and for the Et_2NH/ECA adduct, **12**, also exhibit multiple peaks for the carbonyl and nitrile absorptions. The IR data for the N–H stretch, the C═N stretch, and the C═O stretch and an indication of their intensity for **4**, **10**, **11**, **12**, and the ECA homopolymer are summarized in Table 4.

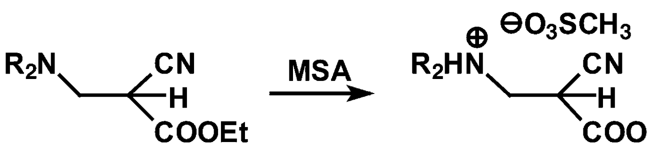
For **11**, the NH stretch absorptions at ca 3400–3500 cm^{-1} are now essentially gone, an indication that both NH protons have reacted with ECA. There are two absorptions for the carbonyl stretch at 1745 and 1665 cm^{-1}, which is similar to what was observed for the $EtNH_2$/ECA adduct, **10**. For the $EtNH_2$/2 ECA adduct, only one absorption is apparent for the nitrile stretch at 2252 cm^{-1}, in contrast to the two absorptions, which are present for the $EtNH_2$/ECA adduct.

The IR data for the Et_2NH/ECA adduct, **12**, is quite similar to that presented for the DMPP/ECA zwitterion, **4**. For adduct **12**, a strong nitrile stretch appears at 2151 cm^{-1} and one of the carbonyl stretches is at 1574 cm^{-1}. This suggests that Et_2NH/ECA adduct, **12**, has a strong zwitterionic contribution to its structure.

3.3. Methanesulfonate salts

To further understand the reason for the complexity of both the NMR and IR data, the amine/ECA adducts were treated with methanesulfonic acid (MSA) to determine if the spectra of the methanesulfonate salts could be more readily interpreted.

The amine/ECA adducts were treated with an equimolar amount of MSA, shown in Eq. (6):



(6)

However, the addition of MSA to the amine/ECA adducts produced only minimal changes in the proton chemical shifts and did little to simplify the ^1H NMR spectra.

The existence of amine/ECA adduct diastereomers also does not explain why the IR spectra are more complicated than expected. The carbonyl absorption for the simple

Table 4
Summary of IR data for **4**, **10**, **11**, **12**, and the ECA homopolymer

Material	N–H (cm^{-1})	C=N (cm^{-1})	C=0 (cm^{-1})
4	–	2145 (s)	1600 (s)
10	3500 (br)	2252 (m) 2148 (w)	1745 (s) 1663 (s)
11	–	2252 (w)	1746 (s) 1665 (s)
12	–	2244 (w) 2151 (s)	1744 (s) 1574 (s)
ECA polymer	–	2247 (w)	1740 (s)

amine/ECA adducts should appear as one peak at ca 1740–1745 cm^{-1}, instead, two peaks are seen in the 1750–1550 cm^{-1} region.

The IR spectra of the amine/ECA/MSA salts did provide more useful structural information when they are compared to the amine/ECA adducts. The addition of MSA to the EtNH$_2$/ECA adduct, **10**, and the EtNH$_2$/2 ECA adduct, **11**, did not significantly affect the nitrile and carbonyl absorptions, as shown in Figs. 7 and 8, respectively.

Unlike the addition of MSA to the zwitterion, **4**, the addition of MSA does not shift or eliminate the nitrile or carbonyl absorptions. Although the nitrile absorption does become weaker, the carbonyl absorptions remain essentially unchanged.

The IR spectrum for Et$_2$NH/ECA/MSA, **15**, is shown in Fig. 9.

In contrast to **10** and **11**, the changes in the IR spectrum of the Et$_2$NH/ECA adduct, **12**, after the MSA addition are much more distinct. The two nitrile absorptions, a weak one at 2244 cm^{-1} and a strong one at 2151 cm^{-1}, become just one weak one at 2250 cm^{-1}. The two carbonyl peaks at 1744 and 1574 cm^{-1}, become a single peak at 1745 cm^{-1}. In this case, the changes are very similar to those which were observed after the addition of MSA to the DMPP/ECA zwitterion, **4**, an indication that the zwitterion must also be present to some extent in **12**.

The complexity of the ^{1}H NMR data, the position of carbonyl and nitrile peaks in the IR spectra, and the changes that occur in the IR spectra after addition of MSA, all suggest that a complex equilibrium must be occurring for the amine/ECA adducts and their MSA salts, as shown in Scheme 1.

The IR data from the amine/ECA adducts indicates that they can exist in three tautomeric forms, zwitterion, **A**, Michael addition adduct, **B**, and enol, **C**. For the EtNH$_2$/ECA adduct, **10**, and the EtNH$_2$/2 ECA adduct, **11**, the absorptions at ca. 1745 and 1645 cm^{-1} correspond to an ester carbonyl and the C=C bond of an enol ether. This implies that Michael addition adduct, **B**, and enol, **C** predominate for **10** and **11**, with little contribution from zwitterion, **A**.

In contrast, the absorptions at 1745 and 1574 cm^{-1} for the Et$_2$NH/ECA adduct, **12**, suggests that **A** and **B** are the major tautomers, with little contribution from enol **C**.

The IR spectra of the methanesulfonate salts confirm these structural assignments. The carbonyl absorptions at ca. 1745 cm^{-1} and ca. 1663 cm^{-1} remain essentially unchanged after **10** and **11** react with MSA to form salts, **13** and **14**. This observation confirms that **10** and **11** exist

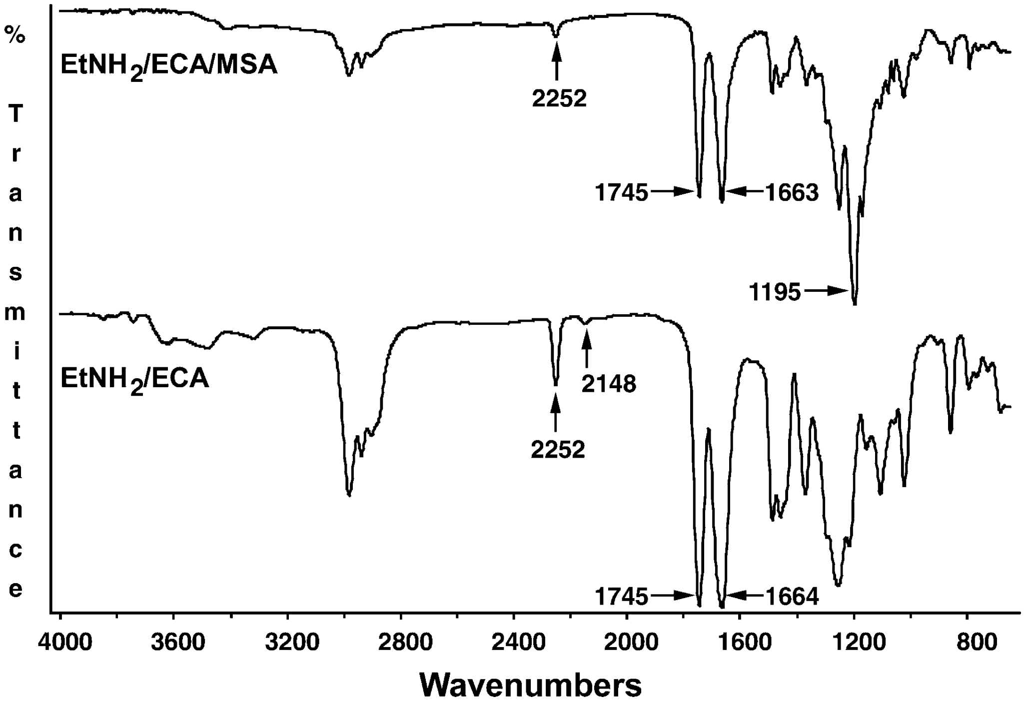


Fig. 7. IR spectra of the EtNH$_2$/ECA adduct, **10**, and EtNH$_2$/ECA/MSA, **13**.

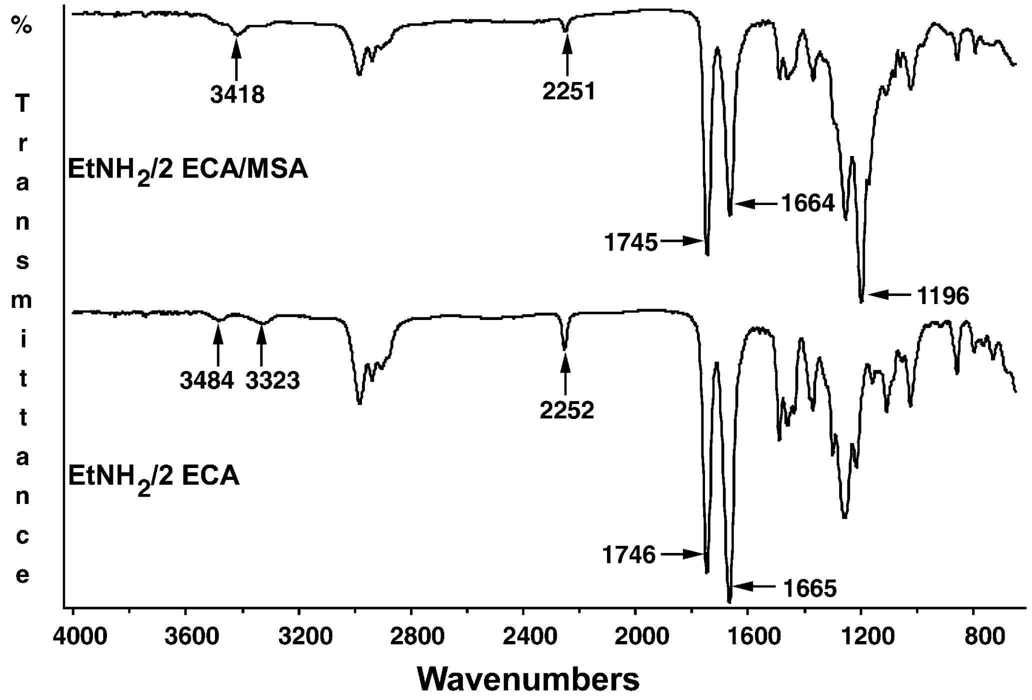


Fig. 8. IR spectra of the EtNH$_2$/2 ECA adduct, **11**, and EtNH$_2$/2 ECA/MSA, **14**.

primarily as **B** and **C**, since **E**, the methanesulfonate salt of **C**, would also be expected to participate in significant hydrogen bonding of the enol tautomer, **E**.

For **12**, significant changes in important peaks of the IR spectrum are observed after reaction with MSA to form salt, **15**. Et$_2$NH/ECA, **12**, exists primarily as structures **A** and **B**. Both tautomers would yield only one product in a reaction with MSA, the methanesulfonate salt, **D**, which what is observed for **15**. There is little or no evidence for the presence of enol, **C**.

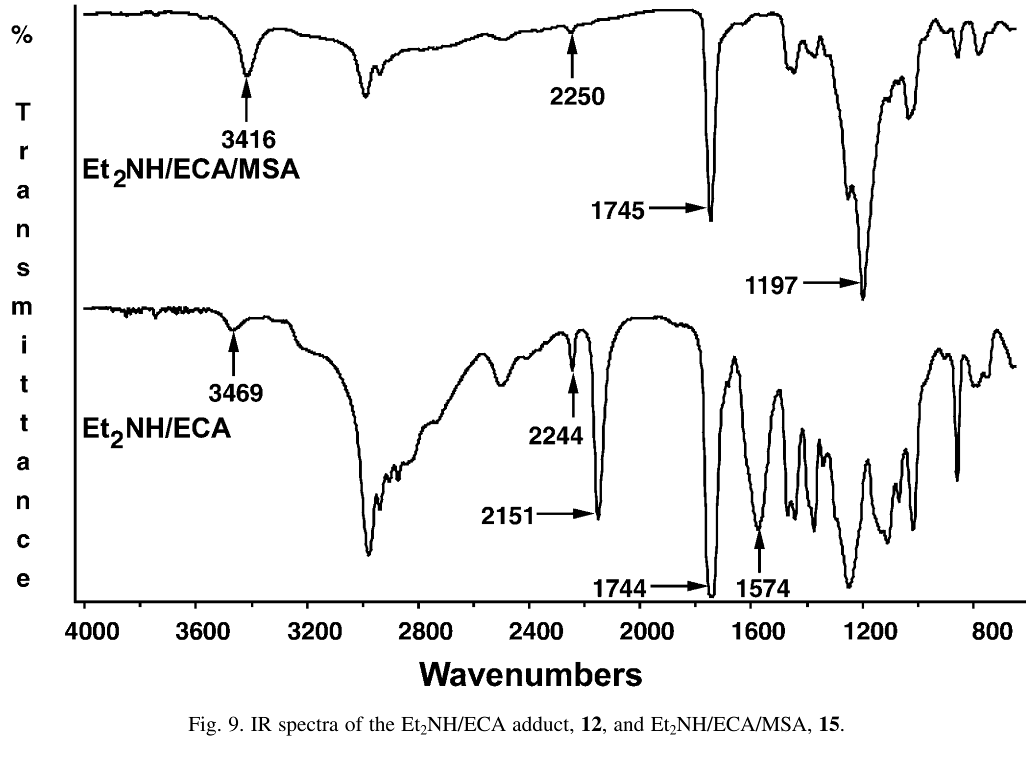
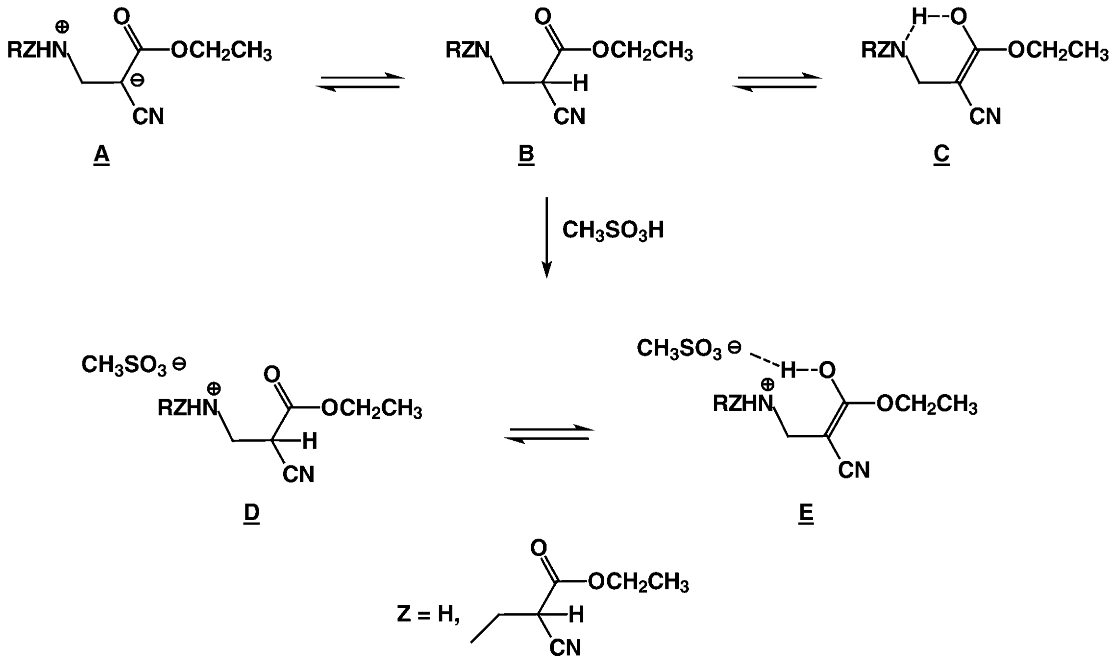


Fig. 9. IR spectra of the Et$_2$NH/ECA adduct, **12**, and Et$_2$NH/ECA/MSA, **15**.



Scheme 1.

4. Conclusions

The proposed zwitterionic initiating species for alkyl cyanoacrylate polymerization has been isolated and fully characterized spectroscopically. DMPP forms a stable zwitterion in a reaction with an equimolar amount of ECA, while the addition of TPP to ECA yields only polymer. Whether this difference in reactivity is primarily a steric or electronic effect is still unclear.

There is also an inherent difference in the reactivity of primary, secondary, and tertiary amines with ECA. Instead of directly initiating ECA polymerization, primary and secondary amines first form aminocyanopropionate esters, because proton transfer occurs after formation of the initial zwitterionic species. A complex equilibrium exists for the reaction products of ECA with primary and secondary amines. The amine/ECA adducts of primary amines exist to a large degree as the enol tautomer and the neutral aminocyanopropionate ester. Secondary amines also form Michael-type addition adducts with ECA, but, in this case, the zwitterion and the neutral ester are the main tautomers, with little evidence for the presence of the enol. Tertiary amines do not possess a proton to transfer, and the reaction of the Michael-type addition adduct with ECA can only initiate polymerization to form high molecular weight adhesive polymer.

While these amine/ECA adducts are tertiary amines, they must be weaker nucleophiles than simple trialkyl amines, because of the contributions of their various tautomers.

This difference in reactivity between the different classes amines explains the difference in the primer performance on polyolefin substrates with ethyl cyanoacrylate based adhesives [12]. Primary and secondary amines first form aminocyanopropionate esters, instead of rapidly initiating the formation of a high molecular weight adhesive polymer. The polymers, which are then initiated by the aminocyanopropionate esters, form at a slower rate and yield lower molecular weight adhesive polymers, which results in lower adhesive bond strengths.

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