

Synthesis of 3-Substituted-2-cyanoacrylates: Their Evaluation as Cross-linkers in Cyanoacrylate Adhesive Compositions

V. VIJAYALAKSHMI, J. N. RUPAVANI, and N. KRISHNAMURTI*

Organic Coatings and Polymers, Indian Institute of Chemical Technology, Hyderabad 500 007, India

SYNOPSIS

Alkyl 2-cyano-2,4-pentadienoates and alkyl 2-cyano-2,4-hexadienoates were synthesized and characterized by spectroscopic methods. These were then evaluated as cross-linkers in 2-cyanoacrylate adhesive compositions to improve the heat stability of their adhesive bonds between various metal surfaces. © 1993 John Wiley & Sons, Inc.

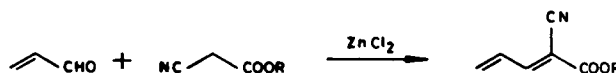
INTRODUCTION

3-Substituted-2-cyanoacrylates have been used from time to time either as cross-linkers for alkyl 2-cyanoacrylates or on their own as adhesives apart from other acrylic monomers. These esters are recommended to use in the alkyl 2-cyanoacrylate adhesive compositions, aiming at improvement of the joint bond strength under higher-temperature conditions.¹⁻⁶ Most of the literature available on their synthesis and their compounding with alkyl 2-cyanoacrylates is in the form of patents that are often misleading. In the present communication, the synthesis of 3-substituted-2-cyanoacrylates such as alkyl 2-cyano-2,4-pentadienoates, and hexadienoates and their effect in alkyl 2-cyanoacrylate adhesive composition on heat aging of adhesive bond strength has been discussed.

EXPERIMENTAL

Synthesis of Alkyl 2-Cyano-2,4-pentadienoates

Different alkyl 2-cyano-2,4-pentadienoates were prepared by reacting corresponding cyanoacetate with acrolein in the presence of a zinc chloride catalyst:

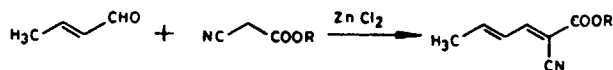


Zinc chloride (0.037 mol) and dioxane (40 mL) were taken in a two-neck round-bottom flask, and this mixture was stirred for about 30 min while heating at 70°C using an oil bath. Then, this mixture was cooled to room temperature (25°C). Alkyl cyanoacetate (0.06 mol) and acrolein (0.075 mol) were added slowly to this mixture. The reaction mixture was stirred for 3 h at 25°C. The product was isolated by taking the product in 50 mL of hexane and further extracting with cold dilute hydrochloric acid in (3 × 100 mL) portions. The organic layer was separated and dried and the solvent removed under reduced pressure. The crude product was recrystallized from a petroleum ether–ethyl ether (1 : 1) mixture. Attempts to check the purity by the GLC technique have failed due to the polymerization of these compounds over the column at 180°C. The purity of the compounds was therefore checked by spectroscopic methods.

Synthesis of Alkyl 2-Cyano-2,4-hexadienoates

Alkyl 2-cyano-2,4-hexadienoates were prepared by reacting crotonaldehyde (0.15 mol) with the corresponding cyanoacetate (0.12 mol) in the presence of a zinc chloride catalyst (0.074 mol) in dioxane (80 mL) as the solvent medium:

* To whom correspondence should be addressed.

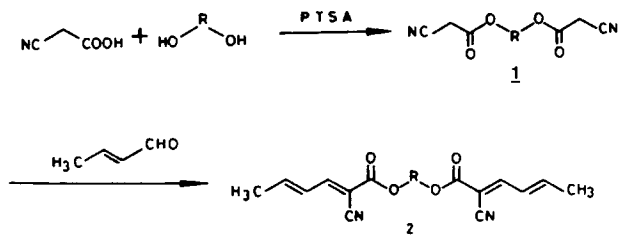


The method of synthesis was similar to that described for pentadienoates.

Synthesis of Alkane Diol

Bis(2-cyano-2,4-hexadienoates)

Alkane diolbis(2-cyano-2,4-hexadienoates) were prepared from alkane dioldicyanoacetates, which were previously prepared from different diols and cyanoacetic acid in the following manner:



Alkane dioldicyanoacetates (**1**) were synthesized by reacting cyanoacetic acid (1.2 mol) with alkane diol (0.5 mol) in the presence of PTSA (1% on reactants) and benzene in an amount equal to the total weight of reactants. The water of the reaction was removed azeotropically using a Dean-Stark trap. After the completion of the reaction, the solvent was removed and the product was dissolved in dichloromethane (DCM) and washed with water several times to remove excess cyanoacetic acid. The crude product was purified by vacuum distillation.

In the second step, zinc chloride (0.029 mol) and dioxane (40 mL) were stirred for 30 min at 80°C. To this alkane dioldicyanoacetate (**1**) (0.02 mol) and crotonaldehyde (0.05 mol) were added slowly after cooling. Then, the reaction mixture was stirred for about 4 h. The temperature was maintained below 30°C until the completion of the reaction. The reaction mixture was extracted with petroleum ether and an ether mixture (1 : 1 w/w) and washed with dil aq HCl; concentration of the solvent followed by recrystallization from ether and hexane in (1 : 1) ratio yielded pure compounds. The purity was checked by spectroscopic methods. Yields (%) and melting points of the 3-substituted-2-cyanoacrylates are reported in Table I.

Table I Yields and Melting Points of 3-Substituted-2-Cyanoacrylates

Compound	Yield (%)	Melting Point (°C)
Alkyl 2-cyano-2,4-pentadienoates		
Methyl	60	40
Ethyl	75	41
<i>t</i> -Butyl	60	60
Alkyl 2-cyano-2,4-hexadienoates		
Methyl	95	58
Ethyl	70	60
<i>t</i> -Butyl	58	74
Propargyl	45	65
Allyl	58	60
3-Chloropropyl	70	62

Characterization of Alkyl 2-Cyano-2,4-pentadienoates and Hexadienoates by Spectroscopy

Infrared (IR) Spectroscopy

The IR spectra were recorded using Perkin-Elmer (Model 221) spectrophotometer. Monomeric esters showed absorption at 2210 cm⁻¹ (for the conjugated CN group) and at 1720–1730 cm⁻¹ (for the conjugated CO group). The two bands in the region 1580–1620 cm⁻¹ are due to the presence of the conjugated butadienoic π-electron system. The absorption bands at 990 to 910 cm⁻¹ are typical of the allyl double bond. The IR spectrum of allyl 2-cyano-2,4-hexadienoate is shown in Figure 1.

¹H-Nuclear Magnetic Resonance Spectroscopy (¹H-NMR)

¹H-NMR spectra were recorded using a Gemini 200 MHz spectrophotometer. Methyl and ethyl 2-cyano-2,4-pentadienoates showed signals of the conjugated butadienoic system doublet at δ 7.65–7.81 for the methyne proton of the group (=CH—CH=CH₂). A multiplet at δ 6.56–7.02 is due to the neighboring methyne proton (=CH=CH—CH=CH₂). The triplet at δ 4.81–6.03 with the integral intensity corresponding to two protons is attributed to methylene protons (=CH—CH=CH₂).

Alkyl 2-cyano-2,4-hexadienoates and bis(2-cyano-2,4-hexadienoates) showed signals of a conjugated butadienoic system multiplet at δ 7.75–7.83 for the methyne proton of the group (—CH—CH=CH—CH₃). The remaining two

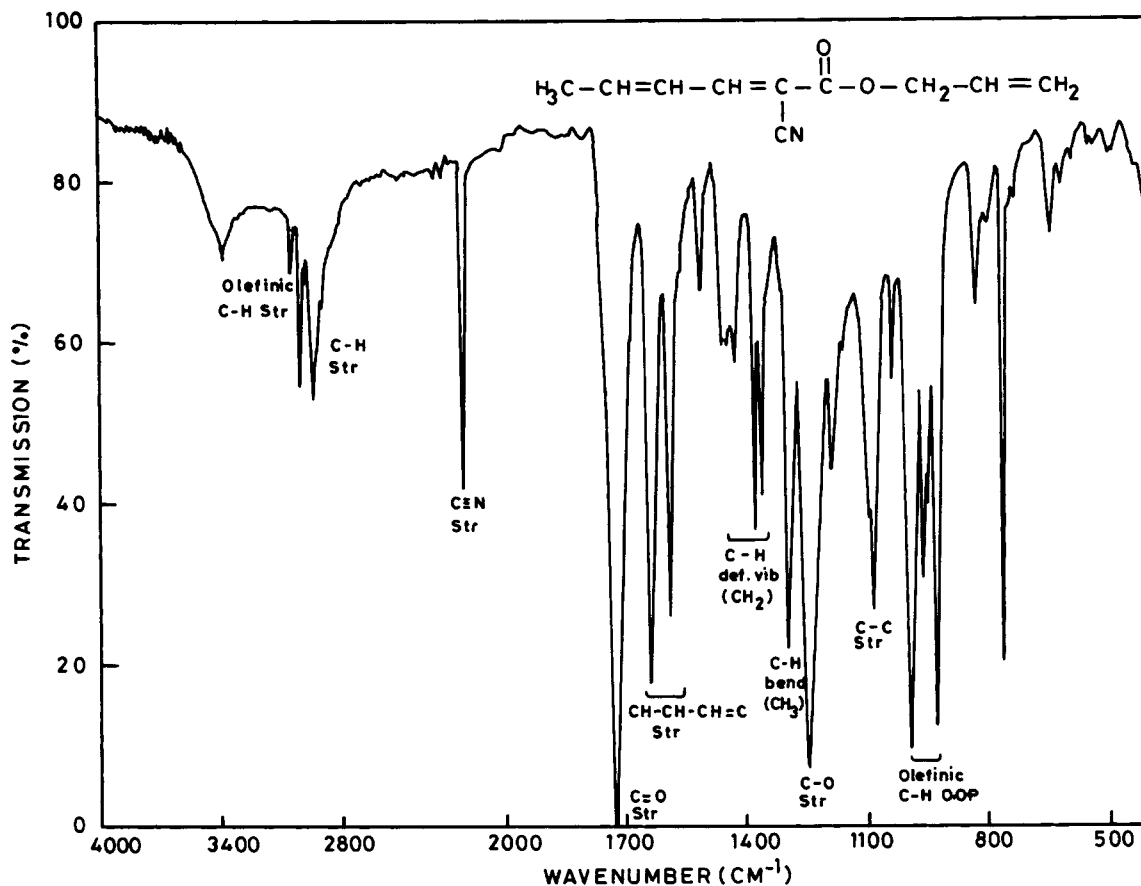


Figure 1 IR spectrum of allyl 2-cyano-2,4-hexadienoate.

methyne protons appeared at δ 6.56–6.68 as a multiplet ($=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$). Protons attached to terminal carbon appeared as doublet at δ 2.02–2.08 ($=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$). Disappearance of the singlet at δ 3.5 corresponding to two protons of cyanoacetate ($\text{NC}-\text{CH}_2-\text{COOR}$) and appearance of the above peaks confirm the formation of dienoates. Detailed spectral data are given in Table II. The ^1H -NMR spectrum of propargyl 2-cyano-2,4-hexadienoate is shown in Figure 2.

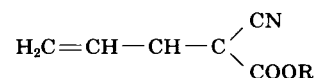
^{13}C -Nuclear Magnetic Resonance Spectroscopy (^{13}C -NMR)

These spectra were recorded using Bruker A.M. 300 MHz spectrophotometer. ^{13}C -NMR spectra of alkyl 2-cyano-2,4-pentadienoates, alkyl 2-cyano-2,4-hexadienoates, and bis(2-cyano-2,4-hexadienoates) are reported now for the first time. ^{13}C -NMR data of the compounds are given in Table III. The ^{13}C -NMR spectrum of 1,4-butanediol bis(2-cyano-2,4-hexadienoate) is shown in Figure 3.

Mass Spectroscopy

Mass spectra of the monomers were recorded using a Micromass VG 7070 U.K. mass spectrophotometer with an electron beam at 70 eV. The important characteristic peaks of the dienoates are shown in Table IV. The mass spectrum of ethyl 2-cyano-2,4-hexadienoate is shown in Figure 4. The base peak is observed at m/z 106 for all alkyl 2-cyano-2,4-pentadienoates. In the case of methyl and ethyl 2-cyano-2,4-hexadienoates, the base peak appeared at m/z 120. For allyl, propargyl, and *t*-butyl 2-cyano-2,4-hexadienoates, R^+ appears as the base peak. Other important fragments are listed below:

Alkyl 2-Cyano-2,4-pentadienoates:



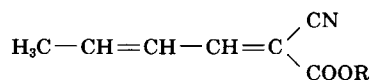
M^+ , $(\text{M}-1)^+$, $(\text{M}-\text{R})^+$, $(\text{M}-\text{HCN})^+$

Alkyl 2-Cyano-2,4-hexadienoates:

Table II $^1\text{H-NMR}$ (δ ppm) Values of 3-Substituted-2-Cyanoacrylates

Alkyl (R)	δ ppm Values of Alkyl Protons
2-Cyano-2,4-pentadienoate	
Methyl	3.81 (s, 3H)
Ethyl	1.20–1.37 (t, 3H, 6), 4.08–4.37 (q, 2H, 6)
<i>t</i> -Butyl	1.61 (s, 9H)
2-Cyano-2,4-hexadienoate	
Methyl	3.87 (s, 3H)
Ethyl	1.25–1.43 (t, 3H, 7), 4.15–4.42 (q, 2H, 7.1)
<i>t</i> -Butyl	1.55 (s, 9H)
Propargyl	2.65–2.71 (t, 1H, 2), 4.81–4.85 (d, 2H, 2)
Allyl	4.71–4.78 (d, 2H, 7), 5.26–5.49 (m, 2H, 4) 5.87–6.08 (m, 1H, 6)
3-Chloropropyl	2.14–2.25 (m, 2H, 5), 3.56–3.75 (t, 2H, 7.5), 4.43–4.46 (t, 2H, 7.2)
Bis(2-cyano-2,4-hexadienoate)	
1,4-Butanediol	1.75–1.87 (t, 4H, 2), 4.18–4.35 (t, 4H, 3.5)
Diethylene glycol	4.35–4.46 (t, 4H, 4), 3.73–3.89 (t, 4H, 5.2)
1,8-Octane diol	1.31–1.39 (m, 12H, 2), 4.2–4.24 (t, 4H, 7.5)

The figures in parentheses are type of signal, no. protons, and J values in Hz.



M^+ , $(\text{M} + 1)^+$, $(\text{M} - 1)^+$, $(\text{M} - \text{R})^+$, $(\text{M} - \text{HCN})^+$

Alkane Diol Bis(2-cyano-2,4-hexadienoates):

1,4-Butanediol : m/z : 328 (M^+), 192, 191 ($\text{M}^+ - \text{C}_7\text{H}_6\text{NO}_2$), 138 ($\text{H}_3\text{C} - \text{CH}=\text{CH} - \text{CH}=\text{C}(\text{CN})\text{COO}^+\text{H}_2$), 55 ($\text{H}_3\text{C} - \text{CH}=\text{CH} - \overset{+}{\text{C}}\text{H}_2$).

1,8-Octanediol : m/z : 384 (M^+), 248 ($\text{M}^+ - \text{C}_7\text{H}_6\text{NO}_2$), 234 ($\text{M}^+ - \text{C}_8\text{H}_8\text{NO}_2$), 206 ($\text{M}^+ - \text{C}_{10}\text{H}_{12}\text{NO}_2$), 111 (110).

3-Substituted-2-cyanoacrylates as Cross-linkers in Cyanoacrylate Adhesive Compositions

Adhesive Formulations

Four different formulations were prepared by adding (10% by weight) methyl 2-cyano-2,4-pentadienoate, ethyl 2-cyano-2,4-pentadienoate, methyl 2-cyano-2,4-hexadienoate, and ethyl 2-cyano-2,4-hexadienoate separately to propyl 2-cyanoacrylate (PCA) adhesive containing (0.03% by weight) hydroquinone and (0.01% by weight) sulfur dioxide. Resultant mixtures were agitated to form a homogeneous mobile adhesive composition. These adhesive formulations were then used for bonding various metal surfaces and their tensile shear strength and impact strength were determined after heat soaking at 25, 100, 125, 150, and 175°C for 1 h. The results are tabulated in Tables V and VI.

Tensile Bond Strength at Different Temperatures

The pi specimens (adherends) were cleaned with fine emery paper and then wiped with dry acetone solvent. Approximately 0.03 mL of adhesive composition was placed on one of the pi specimens and the other one was placed on top of it to spread the adhesive. Glued specimens were left for 24 h at 25°C and then placed in an air oven at different temperatures, as mentioned earlier, for 1 h. Later, the samples were cooled and tested for resistance to a uniform direct pull at 25°C using a tensiometer. Results are given in Table V.

Impact Strength at Different Temperatures

Mild steel blocks were bonded with the adhesive as per ASTM D-950 (78) specification. After 24 h of bonding, the composite unit was placed in an air oven heated to 100, 125, 150, and 175°C for 1 h, cooled, and tested with an impact caused by a pendulum swinging at a known velocity of 335 cm/s along an axis parallel to the glue line.

RESULTS AND DISCUSSION

Synthesis of Alkyl 3-Substituted-2-cyanoacrylates

The synthesis and properties of methyl and ethyl 2-cyano-2,4-pentadienoates have already been described in the literature.⁷ All other monomers synthesized in the present work are new and reported for the first time. These monomers are soluble in aromatic hydrocarbons, chloroform, acetone, and

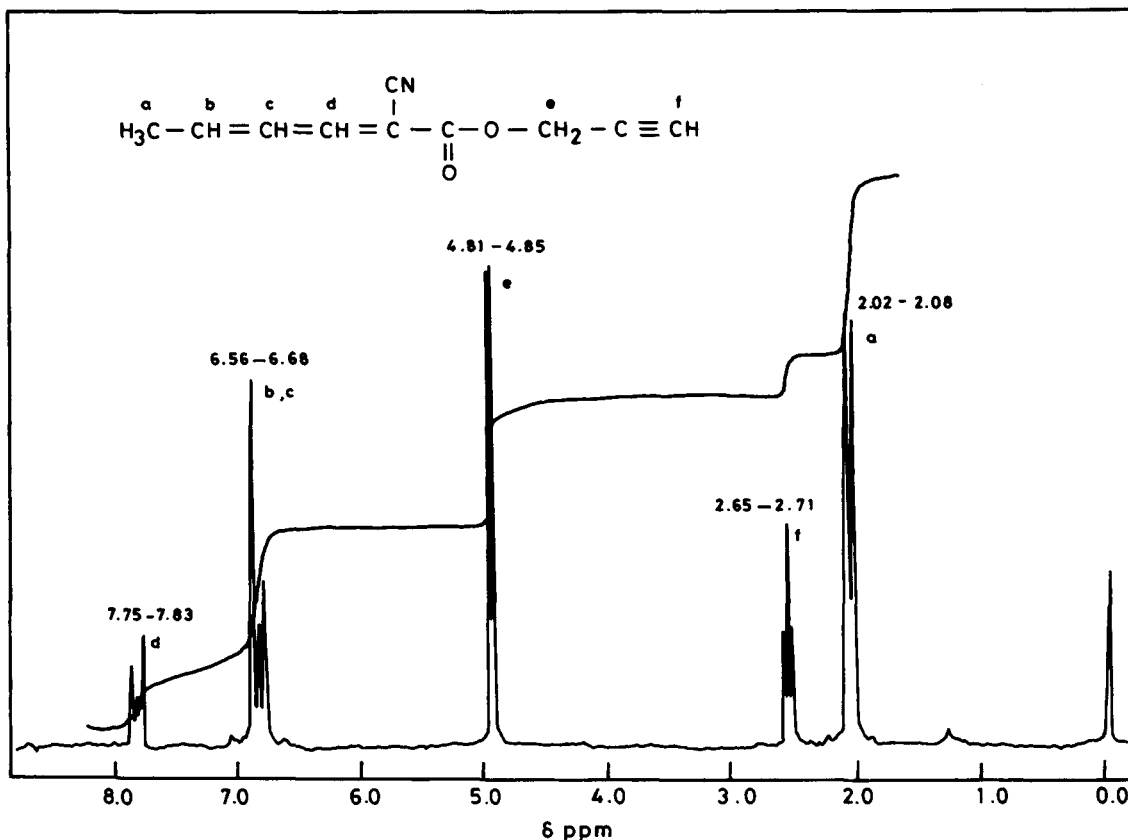
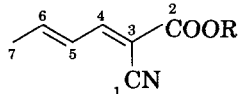
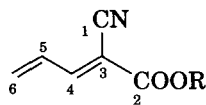


Figure 2 ^1H -NMR spectrum of propargyl 2-cyano-2,4-hexadienoate.

Table III ^{13}C -NMR (δ ppm) Values of 3-Substituted-2-cyanoacrylates

Alkyl 2-cyano-2,4-pentadienoates Alkyl 2-cyano-2,4-hexadienoates



1. 106.16
2. 161.4
3. 113.32
4. 155.03
5. 131.68
6. 134.01

1. 103.5
2. 162.44
3. 114.23
4. 155.88
5. 150.09
6. 127.96
7. 19.19

δ ppm (R)	Alkyl	δ ppm (R')
52.54	Methyl	53.56
13.44, 62.0	Ethyl	13.85, 62.09
—	Propargyl	53.84, 77.26, 78.26
—	Allyl	66.49, 76.58, 77.35

Bis(2-cyano-2,4-hexadienoate)

1,4-Butanediol	24.86, 65.39
1,8-Octanediol	25.58, 28.32, 28.89, 66.19

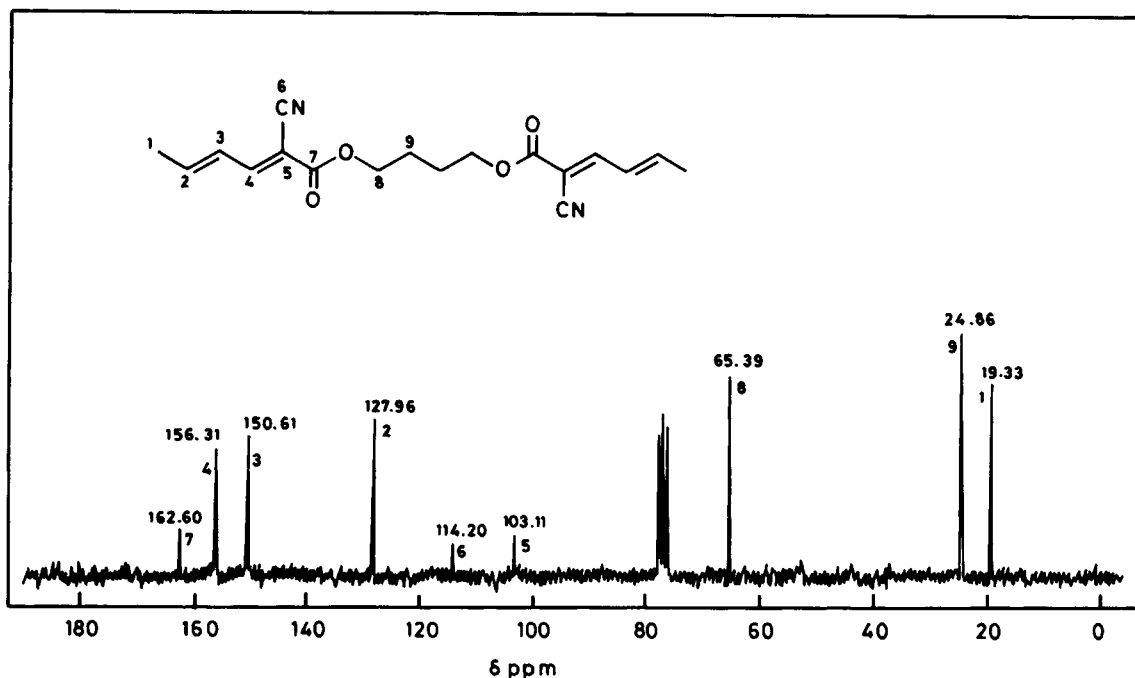


Figure 3 ^{13}C -NMR spectrum of butanediol bis(2-cyano-2,4-hexadienoate).

diethyl ether and sparingly soluble in aliphatic hydrocarbon solvents. In the presence of alcohols, small quantities of water, and organic or inorganic bases, these monomers polymerize, with consider-

Table IV Characteristic Peaks of Fragments in 3-Substituted-2-Cyanoacrylates

Fragment	m/z
<u>Pentadienoates</u>	
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{C} \begin{matrix} \text{CN} \\ \text{CO}^+ \end{matrix}$	106
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{C}^+-\text{CN}$	78
$\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{C}^+$	51
<u>Hexadienoates</u>	
$\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}=\text{C} \begin{matrix} \text{CN} \\ \text{CO}^+ \end{matrix}$	120
$\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}=\text{C}^+-\text{CN}$	92
$\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}^+$	65

able exothermal effect, to form colorless or yellowish rubberlike polymer. This property is probably due to the specific structure of 1,1-disubstituted dienes. The distribution of the π -electron density in their molecule is strongly affected by the combined mesomeric and inductive effect of CN and COOR groups. Therefore, the presence of even a weak base (e.g., OH ion from the dissociation of water molecule) is enough to initiate anionic polymerization. The resulting dienoate anion is stabilized by the two substituents (CN and COOR). Chain propagation is a result of nucleophilic attack of the anionic active end on a monomer molecule.

Tensile Strength at Different Temperatures

Tensile bond strength of unmodified PCA reduced rapidly with increase in the temperature from 25 to 175°C. Addition of 3-substituted-2-cyanoacrylates in PCA increased the bond strength at all temperatures over the unmodified PCA. Addition of these cross-linking agents increased the bond strength up to 150°C and thereafter it reduced (Table V). PCA with alkyl 2-cyano-2,4-pentadienoates showed higher tensile bond strength than did PCA with alkyl 2-cyano-2,4-hexadienoates, i.e., increasing the number of carbons in the diene group decreased the bond strength. The adhesive formulation of PCA with ethyl 2-cyano-2,4-pentadienoate showed more heat resistance than that of those made from dif-

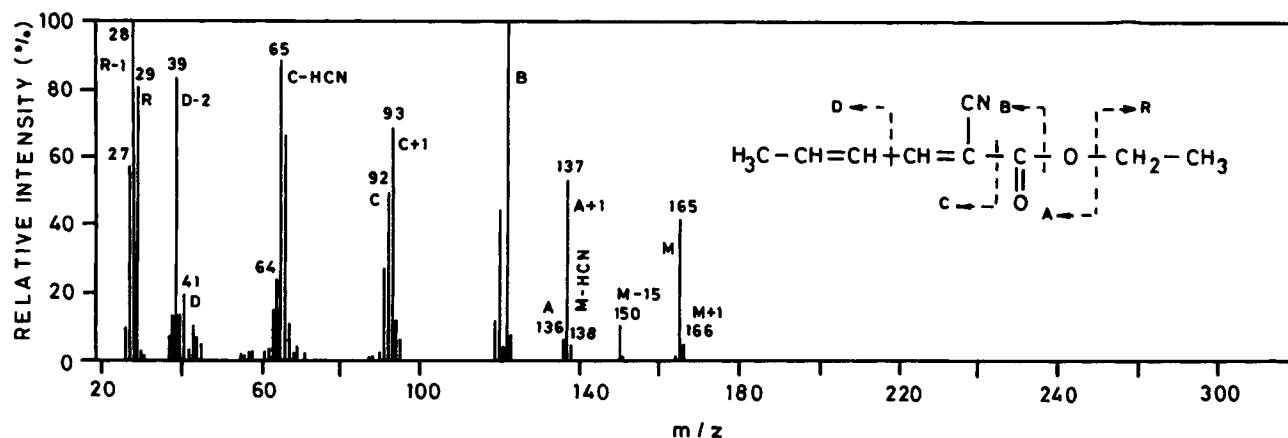


Figure 4 Mass spectrum of ethyl 2-cyano-2,4-hexadienoate.

ferent 3-substituted-2-cyanoacrylates. This could be explained on the basis of degradation studies of the polymer.⁸ Addition of ethyl 2-cyano-2,4-pentadienoate increased the bond strength between stainless-steel surfaces considerably to 22.8 and 25.0 MPa at 100 and 125°C, respectively, as against 8.00 and 6.42 MPa from unmodified PCA. Increase in the

amount of the cross-linking agent from 10 to 20% in PCA showed a very slight increase in the bond strength at higher temperatures.

2-Cyanoacrylate adhesives modified with 3-substituted-2-cyanoacrylates can be used to join surfaces together that are exposed to temperatures in the range from 100 to 150°C. The stability of these

Table V Tensile Bond Strength (MPa) of PCA Containing Different Substituted 2-Cyanoacrylates at Different Temperatures

Adhesives	Adhered Materials	Tensile Strength (MPa)				
		25°C	100°C	125°C	150°C	175°C
PCA + methyl 2-cyano-2,4-pentadienoate	M-M	18.20	20.52	24.30	24.82	6.08
	S-S	20.52	21.30	25.44	25.63	8.35
	A-A	10.64	10.60	12.92	13.42	3.79
	C-C	12.20	12.94	13.76	14.00	3.90
	B-B	12.78	13.84	15.92	16.20	3.42
PCA + methyl 2-cyano-2,4-hexadienoate	M-M	18.20	19.52	22.72	23.00	6.02
	S-S	19.33	20.20	22.90	23.60	7.39
	A-A	9.11	11.22	12.13	13.52	5.31
	C-C	9.11	10.63	12.95	13.47	2.27
	B-B	12.52	13.62	14.43	15.83	2.27
PCA + ethyl 2-cyano-2,4-pentadienoate	M-M	20.51	21.20	24.82	25.20	11.40
	S-S	21.00	22.81	25.00	26.00	15.40
	A-A	11.92	12.22	13.76	13.84	4.56
	C-C	12.51	13.03	13.84	14.03	5.32
	B-B	12.83	15.25	16.72	17.23	6.08
PCA	M-M	12.15	8.29	6.50	2.80	2.66
	S-S	13.65	8.00	6.42	3.12	2.50
	A-A	8.74	6.21	4.23	2.10	1.00
	C-C	10.63	5.10	4.20	2.10	1.00
	B-B	13.22	5.60	4.35	2.50	1.00

M, mild steel; S, stainless steel; A, aluminium; C, copper; B, brass.

Table VI Impact Strength (kJ/m²) of Propyl Cyanoacrylate Containing Different 3-Substituted-2-Cyanoacrylates at Different Temperatures between Mild Steel Surfaces

Adhesives	Impact Strength (kJ/m ²)				
	25°C	100°C	125°C	150°C	175°C
1. PCA + methyl 2-cyano-2,4-pentadienoate	10.2	12.4	15.5	16.0	6.2
2. PCA + methyl 2-cyano-2,4-hexadienoate	9.3	12.4	12.8	13.2	6.0
3. PCA + ethyl 2-cyano-2,4-pentadienoate	12.4	15.5	16.0	16.5	6.8
4. PCA + ethyl 2-cyano-2,4-hexadienoate	9.3	10.4	11.6	11.8	4.6
5. PCA	4.0	1.5	1.0	0.8	0.4

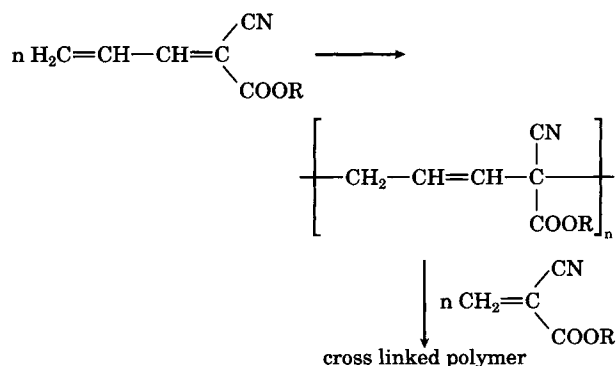
adhesives is also good. The setting times are generally in the range of 10–20 s, depending on the type of surfaces to be joined. The effect of these cross-linking agents depends upon the end group



and unsaturation in the alkyl group. 2-Cyanoacrylate adhesives formulated with 3-substituted-2-cyanoacrylates are found to be resistant to organic solvents and water.

Impact Strength at Different Temperatures

Addition of 3-substituted-2-cyanoacrylates to PCA increased the impact strength substantially at all temperatures over the unmodified PCA. This is due to the stronger bonds, developed due to the cross-linking of 3-substituted-2-cyanoacrylates with PCA. The impact strength increased up to 150°C; thereafter, it reduced (Table VI). The improved heat resistance is attributed to the cross-linking of the residual olefin after the anionic polymerization at 3-substituted-2-cyanoacrylates according to the following equation:



Adhesive formulation of PCA with ethyl 2-cyano-2,4-pentadienoate showed higher impact strength than those made from other 3-substituted-2-cyanoacrylates.

CONCLUSIONS

Addition of alkyl 2-cyano-2,4-pentadienoates to alkyl 2-cyanoacrylates gave improved and heat-resistant (150°C) bonds between various metal surfaces due to the formation of cross-linking polymers. Addition of alkyl 2-cyano-2,4-hexadienoates to alkyl 2-cyanoacrylates also improved the bond strength at higher temperatures, but not as much as those obtained from pentadienoates.

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