

# On the Synthesis and Properties of Some Saturated and Unsaturated Esters of 2-Cyano-2,4-Pentadienoic Acid

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## SYNOPSIS

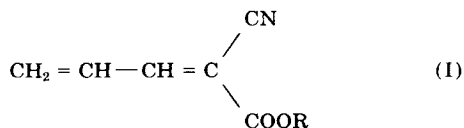
The preparation and properties of some new saturated and unsaturated esters of 2-cyano-2,4-pentadienoic acid (CPDA) are described. A comparison is also made with the known CPDA monomers synthesized under identical conditions. It was found that the monomer yields are dependent on the structure of the corresponding CPDA esters. This fact was explained with solvation effects, occurring during the isolation procedures. The base-catalyzed anionic bulk polymerization of CPDA esters was studied by means of spectral methods. The data indicated that during the homopolymerization 1,4- addition of monomer molecules takes place to give a steric copolymer consisting of 1,4-*cis* and 1,4-*trans* structural units. The ability of poly-CPDA esters was also followed to form crosslinks at room and higher temperatures.

## INTRODUCTION

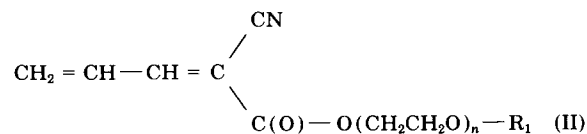
Dienoic compounds used in their monomeric, oligomeric, or polymeric form are well-known objects for studying the ways of increasing the adhesive properties of polymers.<sup>1</sup> Some dienoic derivatives with general formula (I), which were synthesized and characterized for the first time by Gerber,<sup>2</sup> belong also to the same group of compounds.

In recent works<sup>3-6</sup> experiments were described in order to examine CPDA esters as cyanoacrylate adhesive modifiers aiming at improvement of the bonded joint strength under various conditions: raised temperatures, vibrations, high degree of humidity, etc.

The present study deals with the synthesis of new monomeric CPDA esters of the general formula (II). Their preparation conditions and properties were compared with those of similar monomers already known. The anionic bulk polymerization of the CPDA monomers, the structure, and some properties of the obtained polymers were also investigated.



where  $R = \text{alkyl } (C_{1-4})$  or allyl;



where

if  $R_1 = \text{allyl}$ ,  $n = 1$

if  $R_1 = -\text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9,$

$-\text{CH}_2\text{CH}=\text{CH}_2,$   $n = 2$

## EXPERIMENTAL

All monomers were prepared by a published method.<sup>2</sup> The procedure can be summarized as follows: The corresponding cyanoacetic acid ester was reacted with acrolein in mole ratio of 1.25 : 1.0. Dioxane as reaction media and anhydrous  $\text{ZnCl}_2$  as catalyst were applied. The temperature of the continuously stirred reactant mixture was maintained below 30°C up to the complete exhaustion of unreacted ester, which was controlled by means of GC or GPC. The CPDA monomers were isolated from the reaction mixture by extraction with petroleum ether. The combined extracts were treated with di-

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luted aqueous solution of HCl. After separation of the mixture, the organic layer was removed and dried. Finally, the extracting agent was evaporated in vacuum.

The GC studies were performed on a Perkin-Elmer F-17 chromatograph operating with FID and fitted with stainless steel columns being filled with silicon GE XE-60 on Chromosorb W HP DMSC-carrier. A Waters M-590 gel permeation chromatograph with Ultrastayragel columns ( $3 \times 500 \text{ \AA}$  for the monomer samples and  $500, 10^5$ , and  $10^6 \text{ \AA}$  columns for the polymers) was also used.

All gas chromatograms were obtained under the following standard conditions: gas carrier pressure  $250 \text{ kN/m}^2$ ;  $\text{H}_2$  and air pressure  $22.0$  and  $20.0 \text{ kN/m}^2$ , respectively. The injector temperature was  $250^\circ\text{C}$  and the oven temperature  $190^\circ\text{C}$ . The GPC studies were made in THF solutions at  $45^\circ\text{C}$ , a flow rate of  $1 \text{ mL/min}$ , and  $218 \text{ psi}$  pressure in the system.

The IR spectra were made on a Specord M-80 apparatus in a thin layer.  $^1\text{H-NMR}$  investigations were carried out on a JNM PS-100 spectrograph at  $100 \text{ MHz}$  in deuteriochloroform against tetramethylsilane as the internal standard.

The thermogravimetric investigations were performed on a Perkin-Elmer analyzer TGS-2. For the elemental analysis a Tesla C,H,N-automatic analyzer was used.

The necessary polymer CPDA esters were prepared by anionic bulk polymerization of the corresponding monomers, catalyzed by minor quantities

of  $0.1\%$  piperidine solution in acetone. The obtained elastomers were dissolved in acetone, filtered, and precipitated with petroleum ether to remove the unreacted monomer or crosslinked fractions. The polycyanopentadienoates produced by this method were used both for running the  $^1\text{H-NMR}$  or GPC analysis and to investigate the crosslinking at room and higher temperatures. In the last case similar polymer samples were exposed to room temperature or temperatures raised up to  $100^\circ\text{C}$ . Afterwards the treated samples were subjected to extraction with acetone till constant weight of the residue.

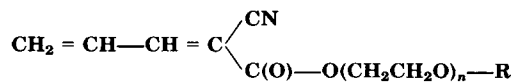
## RESULTS AND DISCUSSION

Table I represents the most important constants of the prepared CPDA monomers. Data about the reaction time, monomer yields, and the purity of the monomers are given in the same table for comparison.

The synthesis and properties of methyl (MCPD), ethyl (ECPD), and *n*-butyl cyanopentadienoate (BCPD) have already been described.<sup>2,3</sup> The preparation of allyl cyanopentadienoate (ACPD) and its properties were not studied in sufficient detail. They are cursorily presented in Ref. 6. All other monomers we have synthesized for the first time.<sup>7</sup>

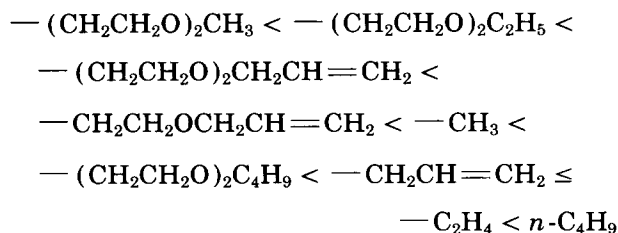
The data in Table I indicate that the monomer yields are dependent on the structure and size of the ester group. On this basis the following order could be made up:

**Table I** Some Physical Properties and Reaction Parameters of Monomer CPDA Esters with General Formula



CPDA Monomer	mp( $^\circ\text{C}$ )	$n_D^{20}$	$d_4^{20}$	GC or GPC* Purity (%)	Retention Time (s)	Reaction Time (h)	Yield, % of Theory <sup>a</sup>
$n = 0, \text{R} = -\text{CH}_3$	45-46	—	—	100	256	8	45
$n = 0, \text{R} = -\text{C}_2\text{H}_5$	39-40	—	—	100	288	8	79
$n = 0, \text{R} = n\text{-C}_4\text{H}_9$	—	1.4842	1.014	97*	1840*	8	86
$n = 0, \text{R} = \text{allyl}$	29-30	—	—	100	367	8	76
$n = 1, \text{R} = \text{allyl}$	—	1.5062	1.071	98	1035	8	46
$n = 2, \text{R} = \text{allyl}$	—	1.4997	1.110	96*	1708*	18	42
$n = 2, \text{R} = -\text{CH}_3$	—	1.4605	1.054	97*	1798*	18	25
$n = 2, \text{R} = -\text{C}_2\text{H}_5$	—	1.4802	1.061	96*	1762*	18	38
$n = 2, \text{R} = n\text{-C}_4\text{H}_9$	—	1.4800	1.038	97*	1726*	18	67

\* Each of the reported values represents the average of five experiments.



It is evident that the yields of the CPDA esters are connected with their solubility in the solvents being used to isolate them from the reaction mixture. The presence of diethylene glycol fragments in the ester radicals was found to cause a decrease of monomer solubility in the nonpolar extracting agent and increase of the same parameter in HCl-aqueous solution, thus reducing the total monomer yields. Obviously, this is due to H-bond formation between ether O atoms and the dipole water molecules. This interaction leads to a large loss of monomer by the washing out of the ether extracts. When a bulky hydrophobic hydrocarbon group is bonded to the DEG fragment, the opposite trend is revealed. That may be attributed to a better monomer solubility in petroleum ether. When dienoate molecules do not include a DEG moiety, an analogous rise of the monomer yields from  $\text{R} = -\text{CH}_3$  to  $\text{R} = n\text{-C}_4\text{H}_9$  is observed. The place of dienoates containing allyl groups may be explained with their medium solubility both in petroleum ether and in HCl-aqueous solution in comparison with the end terms of the discussed order.

From Table I it is also evident that when dienoates with long ester radicals are prepared, a considerably prolonged time to complete the reaction entirely is required. The attempt to reduce the re-

action time to 8 h afforded a reaction product containing 70–75% unreacted ester, which was established by GPC. A possible reason could be the screening of the reaction center (the methylene H atoms) due to a steric hindrance caused by the bulky ester radicals.

Data obtained from the elemental analysis are shown in Table II. A good agreement of the theoretical and practically found results was established which proved the composition of the studied monomers. The structures of the monomer CPDA esters were confirmed by use of IR spectroscopy. The most important spectral data are compared in Table III.

All monomeric CPDA esters exhibit absorption peaks at 2228–2234  $\text{cm}^{-1}$  (for the conjugated CN group) and at 1730–1736  $\text{cm}^{-1}$  (for the conjugated ester C=O group). The two bands in the 1618–1576  $\text{cm}^{-1}$  region showed the presence of the conjugated butadienoic  $\pi$ -electron system. In the spectra of unsaturated CPDA esters, peaks were also detected at 1648  $\text{cm}^{-1}$  and in the region from 990 to 910  $\text{cm}^{-1}$ . They are typical of the allyl double bond. The spectra of monomers containing a DEG fragment showed clear bands in the range of 1075–1120  $\text{cm}^{-1}$ , which is proof for the presence of  $-\text{C}-\text{O}-\text{C}-$  ether bonds.

All monomers were characterized by UV spectroscopy. A typical absorbance at  $\lambda = 261 \pm 1.0$  nm was established. The registered values entirely coincides with the calculated ones on the basis of Woodward–Fieser rule for the K-band of conjugated dienes.<sup>8</sup> The observance of that rule demonstrates that the presence of a bulky ester group does not cause deformation effects or disturbance of the  $\pi$ -electron system, which could have, as a result, a considerable shift towards the higher wavelengths.

**Table II** Elemental Analysis of Monomer Cyanopentadienoates

CPDA Ester	Content of C (%)		Content of H (%)		Content of N (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
ACPD						
( $n = 0$ , R = allyl)	66.25	66.10	5.52	5.53	8.58	8.51
AOEtCPD						
( $n = 1$ , R = allyl)	63.76	62.97	6.32	6.21	6.76	6.64
AOEtEtCPD						
( $n = 2$ , R = allyl)	62.14	61.96	6.82	6.77	5.87	5.78
MEECPD						
( $n = 2$ , R = methyl)	58.66	58.36	6.71	6.50	6.22	6.10
EEECPD						
( $n = 2$ , R = ethyl)	60.24	59.99	7.16	7.00	5.85	5.71
BEECPD						
( $n = 2$ , R = butyl)	62.90	61.98	7.92	7.78	5.24	5.15

**Table III IR Absorption Data of CPDA Esters**

CPDA-monomer	Wavelengths (cm <sup>-1</sup> ) and Vibration Type				
	$\nu_{\text{CN}}$	$\nu_{\text{C=O}}$ ( $\nu_{\text{C=O}}$ )	$\nu_{\text{C=C}}$	$\nu_{\text{C-O-C}}$	$\gamma_{\text{=CH}}$
MEECPD ( $n = 2$ , R = methyl)	2228	1730 (1250)	1618 1578	1080 1115	—
EEECPD ( $n = 2$ , R = ethyl)	2228	1732 (1250)	1620 1582	1075 1120	—
BEECPD ( $n = 2$ , R = butyl)	2228	1735 (1250)	1622 1582	1080 1120	—
ACPD ( $n = 0$ , R = allyl)	2234	1734 (1255)	1618, 1576 1648	1082	969, 915
AOEtCPD ( $n = 1$ , R = allyl)	2227	1736 (1258)	1620, 1578 1648	1090 1120	986 915
AOEtEtCPD ( $n = 2$ , R = allyl)	2230	1735 (1250)	1620, 1582 1648	1080 1120	990, 910

The synthesized monomers were characterized by <sup>1</sup>H-NMR spectroscopy. The obtained data are compared in Table IV.

It is evident that all monomers exhibit signals of the conjugated butadienoic system doublet at 7.75–7.80 ppm for the methyne proton of the group =CH–CH=CH<sub>2</sub>. At  $\delta = 6.80$  ppm was detected a multiple band of the neighbor methyne proton (=CH–CH=CH<sub>2</sub>). In the spectra of unsaturated CPDA esters the peak at  $\delta = 5.84$ –5.88 ppm with integral intensity corresponding to three protons was attributed both to the =CH–CH=CH<sub>2</sub> protons and to the methyne proton of the allyl group in the ester radical (–CH<sub>2</sub>CH=CH<sub>2</sub>). In the spectra of saturated esters on this place only a triple band was

found corresponding to two protons. The methylene protons of the allyl group were detected at  $\delta = 5.25$  ppm.

All spectral data exhibit also a well-expressed triple peak at  $\delta = 4.30$ –4.40 ppm ascribed to the protons of methylene group, which is directly bonded to the carboxyle group. In the ACPD spectrum that signal is shifted to 4.70 ppm due to the effects of the terminal double bond of the neighbor allyl group.

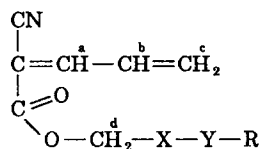
Dienoates containing EG or DEG fragment showed a multiple band at 3.58–3.70 ppm. They are characteristic for the “middle” methylene protons of the –CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O– link.

In the spectra of CPDA monomers, signals were also detected corresponding to the alkyloxy terminal

**Table IV Chemical Shifts ( $\delta$ , ppm) of Methyne and Methylene Protons in the CPDA Esters**

Dienoate	R	$\delta$ (ppm)					
		a	b	c	d	e	f + g
ACPD	Allyl	7.80	6.80	5.84	4.70	—	—
AOEtCPD	Allyl	7.80	6.80	5.86	4.36	3.68	—
AOEtEtCPD	Allyl	7.85	6.80	5.88	4.40	—	3.70
MEECPD	Methyl	7.76	6.80	5.88	4.30	—	3.60
EEECPD	Ethyl	7.78	6.80	5.88	4.32	—	3.62
BEECPD	<i>n</i> -Butyl	7.76	6.80	5.86	4.30	—	3.58

X = –CH<sub>2</sub>O–; Y = –CH<sub>2</sub>CH<sub>2</sub>O–.

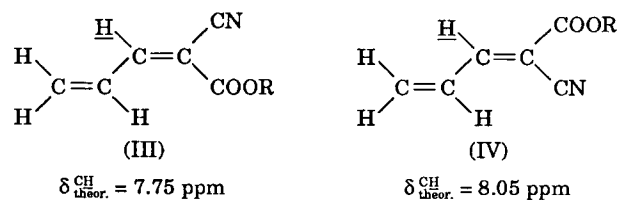


**Table V** Chemical Shifts ( $\delta$ , ppm) of the Protons in the Ester Groups

R	$-\text{CH}_3$	$-\text{CH}_2\text{CH}_3$	$-(\text{CH}_2)_2-\text{CH}_3$		$\text{Y}-\text{CH}_2-\text{CH}=\text{CH}_2$		
$\delta$ (ppm)	3.28	1.15	1.40	0.82	3.90	5.89	5.25

groups (Table V). For the  $-\text{OCH}_3-$  group there is a single band at  $\delta = 3.30$  ppm. The considerable shift towards the weak fields is caused by the direct bonding to O atom. The methyl protons of the ethoxy end group were registered at  $\delta = 1.14$  ppm (a triple band) and the same protons in the *n*-butyl group at  $\delta = 0.8$  ppm. The non-well-split multiple peak at  $\delta = 1.40$  ppm was attributed to the  $-\text{CH}_2\text{CH}_2-$  protons of the *n*- $\text{C}_4\text{H}_9$  group.

In all six  $^1\text{H-NMR}$  spectra the registered integral intensities corresponded to the number of protons, as expected according to the molecular formula. In order to evaluate the combined action of several substituents by chemical shift determination in the  $^1\text{H-NMR}$  spectra of CPDA monomers, some empirical additive models were employed.<sup>9,10</sup> That afforded a precise interpretation of the spectra as well as determination of the spacial location of the CN- and  $-\text{COOR}-$  groups with respect to the conjugated system. There are two possible structures (III and IV) with different chemical shifts of the marked methyne proton:



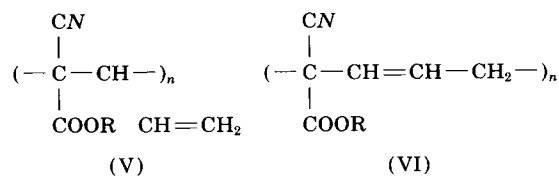
As previously mentioned, the practically found chemical shift of this type protons is in the range of 7.75–7.80 ppm for all CPDA monomers. This fact indicates that in monomeric state structure (III) is preferred, which is probably more advantageous from the energetic point of view and does not depend on the ester radical size.

All synthesized monomer CPDA-esters are well soluble in aromatic hydrocarbons, chloroform, acetone, and diethylether and sparingly soluble in petroleum ether, heptane, hexane, etc. In the presence of alcohols, small quantities of water, organic or inorganic bases, they polymerize with considerable exothermal effect to form colorless or yellowish rubberlike polymers. That property is probably due to the specific structure of 1,1-disubstituted dienes. The distribution of the  $\pi$ -electron system density in their

molecules is strongly affected by the combined mesomeric and induction influence of the  $-\text{CN}$  and  $-\text{COOR}$  substituents. So the presence even of a weak base (e.g., OH ion from the dissociation of water molecules) is enough to initiate an anionic polymerization process. The resulting dienate anion is stabilized by the two substituents. The chain propagation is a result of nucleophilic attack of the anionic active end on a monomer molecule. This type of initiation and propagation is typical of anionic polymerization.

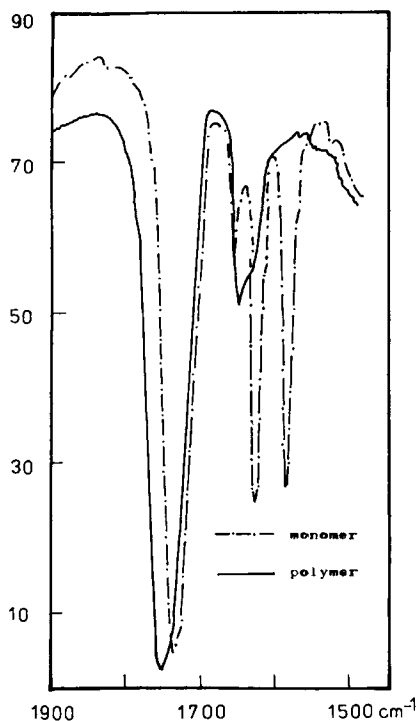
It is well known that 1,3-butadiene, when polymerized by the use of alkali metals or Ziegler-Natta catalytic systems, can form two different polymer structures. The first one is obtained after 1,2-addition of the monomer molecules and contains a vinyl group in the side chain. The other one is a result of 1,4-addition and is characterized by the presence of double bond in the main chain with possibilities for *cis-trans* isomerization.<sup>11</sup>

Based on general considerations, it could be predicted that the 1,1-disubstituted butadiene derivatives will polymerize analogously, forming steric copolymers containing both 1,2- and 1,4- *trans* or *cis* structural units (V) and (VI):



There are no data or studies concerning the mechanism of disubstituted dienoates polymerization or the structure and properties of polymeric CPDA esters. In order to help clarify that problem, IR, UV and  $^1\text{H-NMR}$  spectroscopic methods were used.

In Figure 1 the IR spectra of AOEtCPD and that of the corresponding polymer are compared. Poly-AOEtCPD was produced when the monomer was left to stand between the NaCl windows of an IR cell 24 h long at room temperature without addition of a catalyst. It could be seen that the symmetric doublet at 1618,1582  $\text{cm}^{-1}$ , caused by the presence of conjugated double bonds transits into a single ab-



**Figure 1** IR spectra comparison of AOEtCPD and poly-AOEtCPD.

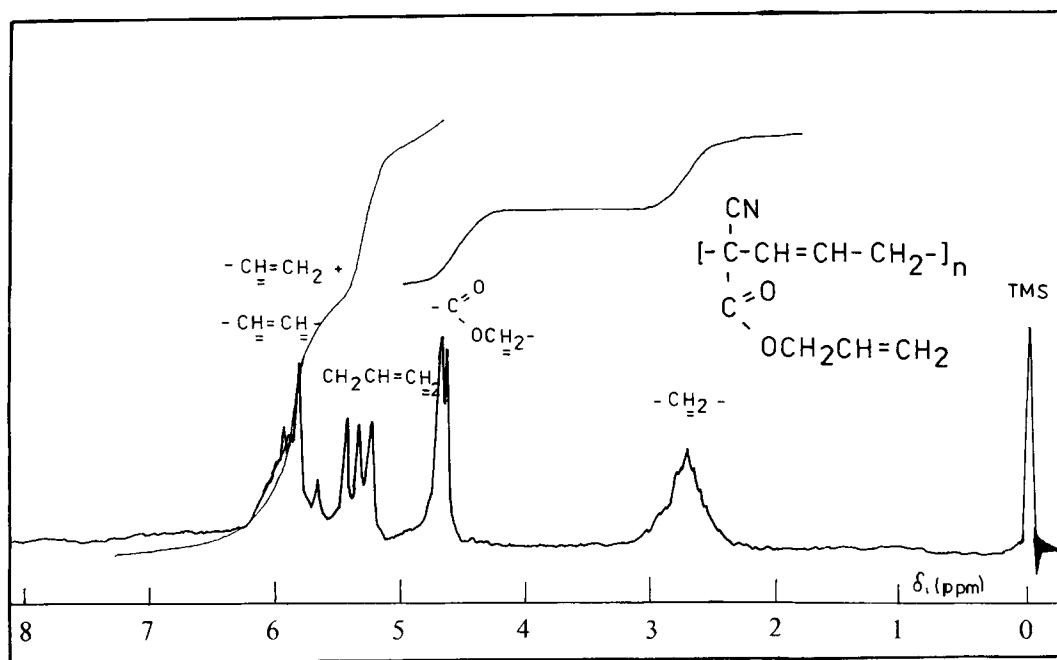
sorption peak at  $1648\text{ cm}^{-1}$  determining the presence of isolated double bond. Furthermore, the band at  $1730\text{ cm}^{-1}$  of the conjugated ester carbonyl group moves about  $20\text{ cm}^{-1}$  towards the greater wave-

lengths. The resulting value is typical of unconjugated esters. An analogous trend is revealed for the CN band, too.

The IR spectral data confirmed the propositions about the polymerization of 1,1-disubstituted dienes. The UV spectrum of the obtained polymers showed that the absorption at 261 nm characterizing the K-band of the conjugated system is presented no longer.

$^1\text{H-NMR}$  spectrum of poly-ACPD is shown in Figure 2. There are no signals above 6.2 ppm, which proves the absence of conjugated double bonds, thereby confirming that the polymerization proceeds with destruction of the dienoic system. The location and the shape of the signals at 4.65 and 5.30 ppm, corresponding to methylene protons of the allyl group ( $-\text{OCH}_2\text{CH}-$  and  $-\text{CH}=\text{CH}_2$ ) are the same as in the spectrum of the starting monomer (Fig. 3). However, the peak at  $\delta = 5.75\text{ ppm}$  is with disturbed fine structure and has integral intensity corresponding to three protons. It is most probably that this effect is due to a signal overlapping of the allyl group methyne proton with the signals of other two protons unshielded approximately in the same degree. These are probably the protons of the structure  $-\text{CH}=\text{CH}-$ , being realized only in the case of 1,4-addition.

The signal registered at 2.7 ppm with integral intensity corresponding to two protons corroborates that statement. Most probably these protons are of



**Figure 2**  $^1\text{H-NMR}$  spectrum of poly-ACPD.

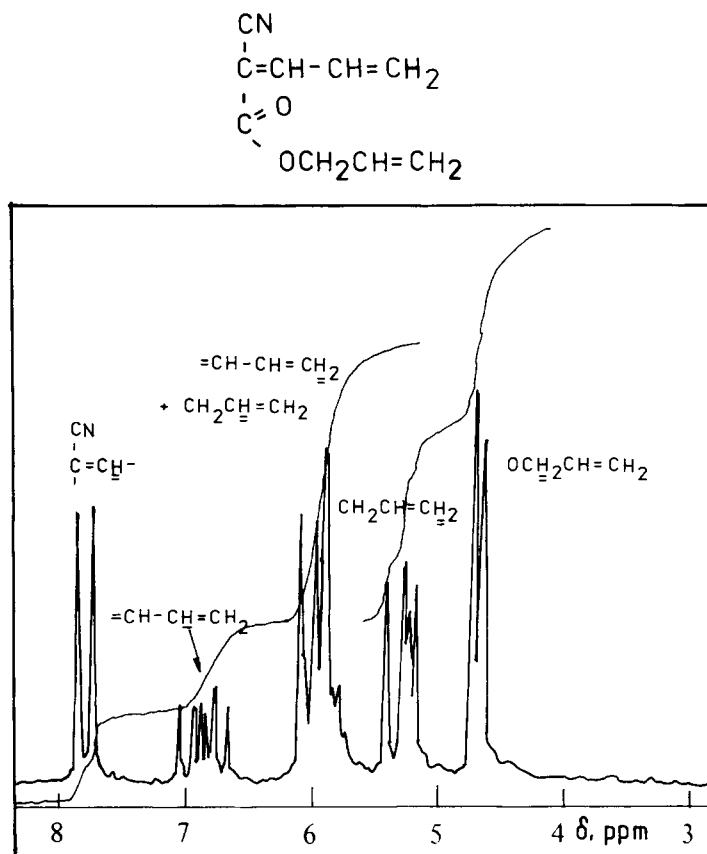


Figure 3  $^1\text{H-NMR}$  spectra of ACPD.

the  $-\text{CH}_2-$  type of structure typical only for 1,4-addition of monomer units.

Analyzing the  $^1\text{H-NMR}$  spectrum of poly-ACPD in comparison with those of ACPD, we concluded that at the conditions of anionic polymerization 1,4-addition took place without affecting the double bond in the ester group.

Aiming a most precise investigation of the monomer units addition involved IR spectroscopy. There are a great deal of spectral studies concerning the structure of unsubstituted 1,3-polybutadiene. In the spectra of each polybutadiene isomer (1,2-, 1,4- *cis* or *trans*), strong characteristic absorption peaks were detected at the following wavelengths<sup>12,13</sup>:

for 1,2-isomer	at $910\text{ cm}^{-1}$
for <i>trans</i> -1,4-isomer	at $967\text{ cm}^{-1}$
for <i>cis</i> -1,4-isomer	at $750\text{ cm}^{-1}$

It has been found that the  $1630\text{--}1670\text{ cm}^{-1}$  range is characteristic, too. The *cis*-  $-\text{CH}=\text{CH}-$  structure absorbs at  $1630\text{--}1660\text{ cm}^{-1}$  and the *trans*-1,4

structure at  $1660\text{--}1678\text{ cm}^{-1}$ . In the last case a peak at about  $3025\text{ cm}^{-1}$  should also be presented. The characteristic absorption bands of vinyl group which is typical for 1,2- addition have been registered at  $3077, 1648, 998,$  and  $910\text{ cm}^{-1}$ . This fact allows a clear distinction from the  $-\text{CH}=\text{CH}-$  structure.<sup>13</sup>

As a model compound for our IR investigations poly-MCPD was chosen. The polymer was prepared by polymerization of the corresponding monomer between the windows of a IR spectroscopic cell. The obtained spectra are depicted in Figure 4. Bands at  $970$  and  $760\text{ cm}^{-1}$  were detected, thus proving 1,4-addition of the molecules. Furthermore, the clear absorption maximum at  $3025\text{ cm}^{-1}$  and the two bands registered at  $1654.0$  and  $1665.6\text{ cm}^{-1}$  are in good agreement with the 1,4- addition model.

All spectral data obtained indicated that no peaks are observed for vinyl group. On this basis we can conclude that under the conditions of polymer preparation in our case 1,2- addition does not proceed.

Similar data were obtained when the other poly-cyanopentadienoates were studied. In the range from  $1000$  to  $700\text{ cm}^{-1}$  the deviations from the values already being registered are negligible up to  $5\text{ cm}^{-1}$ .

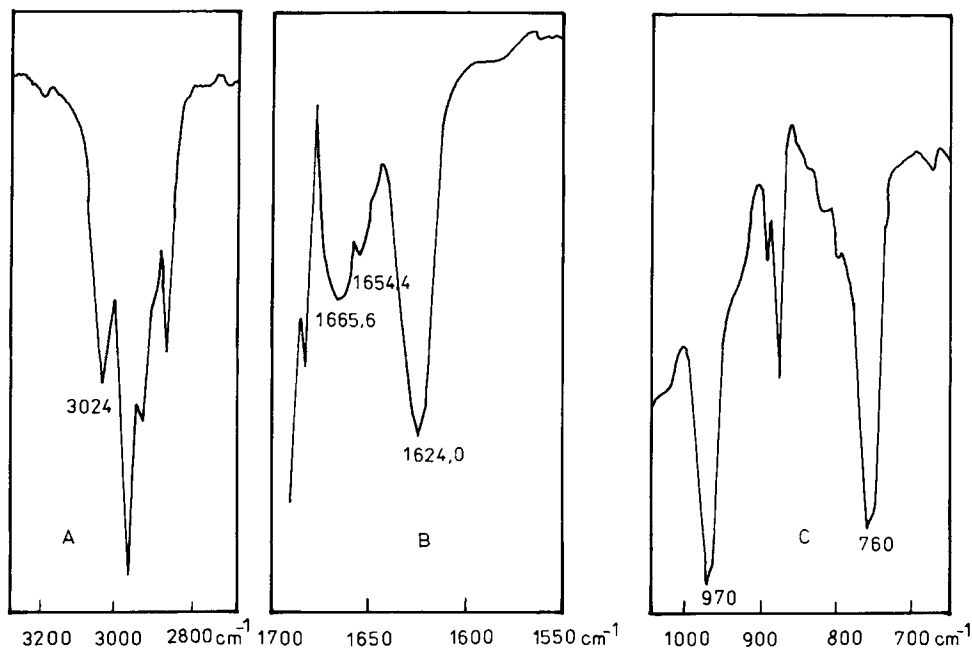


Figure 4 IR spectra of poly-MCPD in the studied characteristic ranges.

This fact indicates that the ester radical length does not affect the type of monomer units addition.

The difference in the chemical structure of saturated and unsaturated polymer CPDA esters defines their different behavior at higher temperatures. In Figure 5 the thermogravimetric curves of destruction of two CPDA polymers are compared. The bimodality of the curve, characterizing the unsaturated CPDA ester, may be attributed to the different type of destruction taking place in this case. The second section beginning from about 40% weight loss was ascribed to thermodestruction of crosslinked products formed probably after reaction of the allyl double bond caused by the raised temperatures.

In order to prove the supposed crosslinking of the CPDA polymers, gelation experiments were carried out. Samples from poly-ACPD, poly-AOEtCPD, and poly-AOEtEtCPD were extracted with acetone till constant weight of the residue before and after a heat treatment at 110°C for 24 h. Here a comparison of the properties of poly-ECPD and the said polymers was appropriate. All data from gelation experiments are given in Table VI.

It is evident that, in the case of unsaturated poly-CPDA esters, intensive crosslinking occurs even at room temperature. That structural change is obviously due to reaction of the allyl double bond. Making a comparison between the gelation experiments data obtained for poly-ECPD and for the

other three polymers, an assumption can be made that the double bond in the main chain reacts only at higher temperatures and in a lower degree. When unsaturated poly-CPDA esters were examined, the crosslinking after heat treatment may be attributed to simultaneous reaction both of the allyl and of the substituted  $-\text{CH}=\text{CH}-$  bonds.

## CONCLUSIONS

Nine monomer CPDA esters with various length and structure in the ester groups were synthesized and

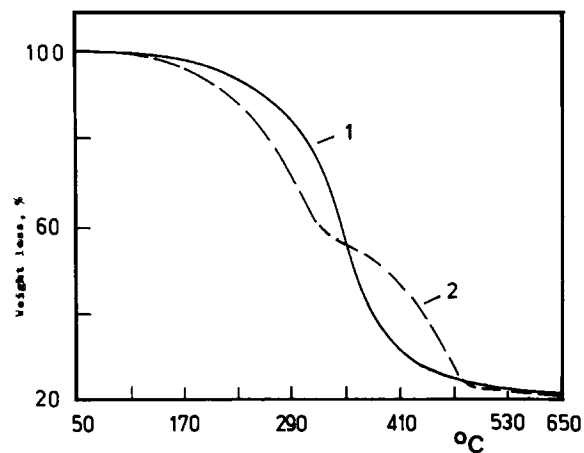


Figure 5 Thermogravimetric curves of destruction of poly-EEEECPD (1) and poly-AOEtEtCPD (2) at heating rate of 20°C/min.



**Table VI Gel-Fraction Quantity before and after Thermal Treatment of Various poly-CPDA Polymers**

Polymer CPDA Ester	Gel Fraction Quantity (wt %) after 20 Days at 23–25°C	Gel Fraction Quantity (wt %) after 24 h at 110°C	Weight Loss of the Samples after Heat Treatment (%)
Poly-ECPD	0.3	52.5	0.20
Poly-ACPD	72.2	80.0	1.30
Poly-AOEtCPD	83.0	95.5	0.29
Poly-AOEtEtCPD	73.0	85.5	0.14

characterized. It was established that the changes of the ester radical length and composition affect considerably the physical properties of the monomers, but a significant influence on the type of monomer units addition during the anionic polymerization was not found.

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