Die Angewandte Makromolekulare Chemie **92** *(1980) 41–52 (Nr. 1421)*

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Synthesis and Properties of Some Alkenyl- and Alkinyl-2-Cyanoacrylates

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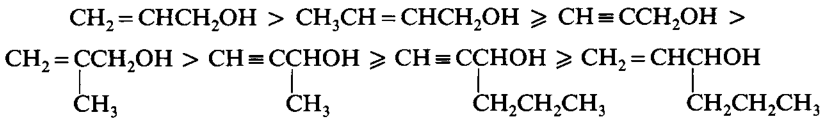
(Received 8 February 1980)

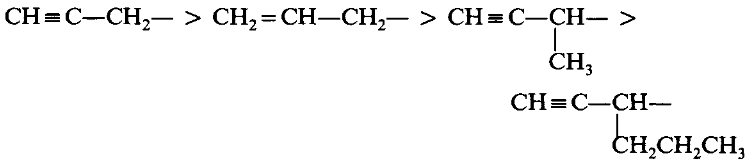
SUMMARY:

Some alkenyl- and alkinyl-2-cyanoacrylate monomers, possessing adhesive properties were synthesized. The ease of esterification of cyanoacetic acid, the first step of the synthesis, with some alcohols was in the following order:



$$CH_2{=}CHCH_2OH > CH_3CH{=}CHCH_2OH \geqslant CH{\equiv}CCH_2OH > CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2OH > CH{\equiv}C\underset{\displaystyle CH_3}{\underset{|}{C}}HOH \geqslant CH{\equiv}C\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{C}}HOH \geqslant CH_2{=}CH\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{C}}HOH$$

After condensation of the cyanoacetates with formaldehyde to low molecular weight polymers and depolymerization in vacuum, allyl-2-cyanoacrylate, propargyl-2-cyanoacrylate, 1-methyl-2-propinyl-2-cyanoacrylate and 1-propyl-2-propinyl-2-cyanoacrylate were obtained, the last two for the first time. It was found that the strength of the adhesive bonds of these monomers depends primarily on the number of C atoms in the ester group of the molecule, i.e.

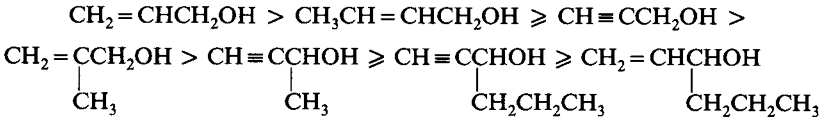


$$CH{\equiv}C\text{—}CH_2\text{—} > CH_2{=}CH\text{—}CH_2\text{—} > CH{\equiv}C\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—} > CH{\equiv}C\text{—}\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{CH}}\text{—}$$

The introduction of double and triple bonds increases the tensile strength properties. The unsaturated cyanoacrylates also have a better heat-resistance of their bonds: $CH_2{=}CHCH_2\text{—} > CH{\equiv}CCH_2\text{—} > CH{\equiv}CC(CH_3)H\text{—} > CH{\equiv}CC(C_3H_7)H\text{—} >$ alkyl. This result is explained with the formation of cross-links in the adhesive layer, confirmed by IR and thermogravimetric data.

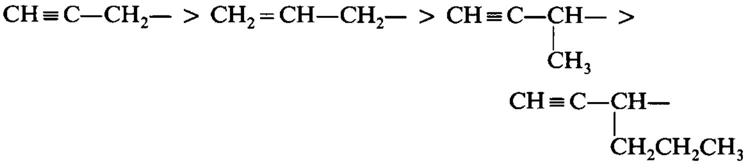
ZUSAMMENFASSUNG:

Einige Alkenyl- und Alkinyl-2-cyanacrylatmonomere, die Eigenschaften eines Klebstoffs besitzen, wurden synthetisiert. Die erste Stufe der Synthese war die Veresterung der Cyanessigsäure mit einigen Alkoholen. Für die Leichtigkeit der Veresterung ergab sich die Reihenfolge:



$$\mathrm{CH_2{=}CHCH_2OH > CH_3CH{=}CHCH_2OH \geqslant CH{\equiv}CCH_2OH >}$$
$$\mathrm{CH_2{=}\underset{CH_3}{C}CH_2OH > CH{\equiv}C\underset{CH_3}{C}HOH \geqslant CH{\equiv}C\underset{CH_2CH_2CH_3}{C}HOH \geqslant CH_2{=}CH\underset{CH_2CH_2CH_3}{C}HOH}$$

Nach der Kondensation der Cyanacetate mit Formaldehyd zu Polymeren niedrigeren Molekulargewichts und Depolymerisation im Vakuum wurden Allyl-2-cyanacrylat, Propargyl-2-cyanacrylat, 1-Methyl-2-propinyl-2-cyanacrylat und 1-Propyl-2-propinyl-2-cyanacrylat synthetisiert — dabei die letzten zwei zum ersten Mal. Es wurde gefunden, daß die Festigkeit der Klebstoffverbindung hauptsächlich von der Zahl der C-Atome der Estergruppe des Moleküls abhängig war:



$$\mathrm{CH{\equiv}C{-}CH_2{-} > CH_2{=}CH{-}CH_2{-} > CH{\equiv}C{-}\underset{CH_3}{C}H{-} > CH{\equiv}C{-}\underset{CH_2CH_2CH_3}{C}H{-}}$$

Die Einführung von Doppel- und Dreifachbindungen erhöhte die Festigkeit. Ungesättigte Cyanacrylate zeigten eine bessere Temperaturbeständigkeit der Klebstoffverbindung: $\mathrm{CH_2{=}CHCH_2{-} > CH{\equiv}CCH_2{-} > CH{\equiv}CC(CH_3)H{-} > CH{\equiv}CC(C_3H_7)H{-}}$ > Alkyl. Dies wurde durch die Bildung einer Vernetzung in der Klebstoffschicht erklärt. Dabei wurden IR und TG Analysen herangezogen.

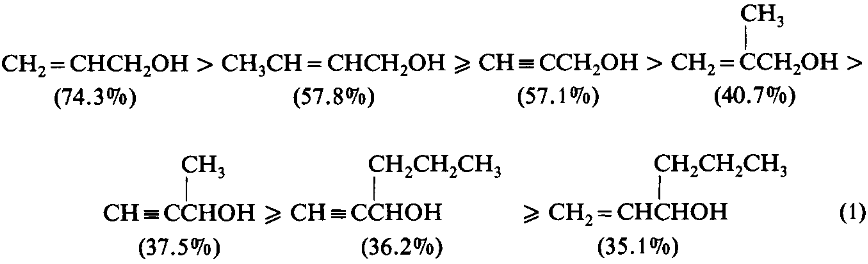
Introduction

The alkyl esters of 2-cyanoacrylic acid have found a unique application as instant curing adhesives for various substrates, ranging from metals and plastics to living tissue. A strong adhesive bond is achieved at room temperature, without use of catalysts or pressure, for an extremely short period — several seconds to several minutes. The adhesive action is a result of exothermal anionic polymerization, initiated by water molecules adsorbed on the object's surface[1]. A main deterrent for the use in industrial assemblage is the low temperature resistance (80 °C) of the alkyl-2-cyanoacrylates' bonded joints.

One way to improve the heat-resistance of these adhesives is to synthesize unsaturated 2-cyanoacrylate monomers. It is presumed that after anionic curing they would be able to undergo a heat-initiated radical polymerization, yielding a three-dimensional adhesive layer with improved thermal properties[2,3]. The study of the correlation between structure and heat-resistant properties of unsaturated cyanoacrylates is of both scientific and technical interest and is the object of the present paper.

Results and Discussion

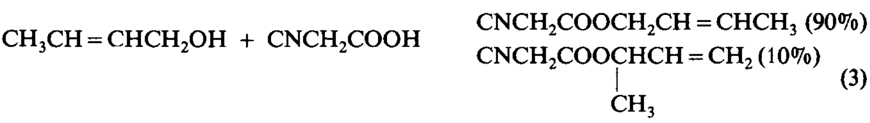
The first step of the cyanoacrylate synthesis was the preparation of the corresponding cyanoacetates. They were obtained by direct esterification of cyanoacetic acid with alcohols, the ease of esterification being in the following order (the percentage in parentheses is the yield of cyanoacetate):



$$\underset{(74.3\%)}{CH_2{=}CHCH_2OH} > \underset{(57.8\%)}{CH_3CH{=}CHCH_2OH} \geqslant \underset{(57.1\%)}{CH{\equiv}CCH_2OH} > \underset{(40.7\%)}{CH_2{=}\overset{\overset{CH_3}{|}}{C}CH_2OH} > \underset{(37.5\%)}{CH{\equiv}\overset{\overset{CH_3}{|}}{C}HOH} \geqslant \underset{(36.2\%)}{CH{\equiv}\overset{\overset{CH_2CH_2CH_3}{|}}{C}HOH} \geqslant \underset{(35.1\%)}{CH_2{=}CH\overset{\overset{CH_2CH_2CH_3}{|}}{C}HOH} \qquad (1)$$

The physical properties, gas-chromatographic[4] and CHN data are reported in Tab. 1. IR spectra also confirm the above mentioned cyanoacetates. The gas-chromatograms of 2-butenyl-cyanoacetate and 1-propyl-2-propenyl-cyanoacetate showed the presence of another compound in a quantity of about 10%. As this compound shows the same data in elementary analysis it was suggested to be an isomer. Because of electromeric resonance, the hydroxyl group of the allyl alcohols is mobile:

$$CH_3CH{=}CH_2OH \rightleftharpoons {}^{-}OH + [CH_3CH{=}CH\overset{+}{C}H_2 \leftrightarrow CH_3\overset{+}{C}HCH{=}CH_2] \qquad (2)$$



$$CH_3CH{=}CHCH_2OH + CNCH_2COOH \quad \begin{array}{l} CNCH_2COOCH_2CH{=}CHCH_3\ (90\%) \\ CNCH_2COO\underset{\underset{CH_3}{|}}{C}HCH{=}CH_2\ (10\%) \end{array} \qquad (3)$$

Such isomerization should be possible in the formation of only 2-butenyl-cyanoacetate and 1-propyl-2-propenyl-cyanoacetate. Some cyanoacetates were condensed with formaldehyde to low molecular weight polymers. Thermal depolymerization in vacuum released the alkenyl- and alkinyl-

Tab. 1. Physical properties, elementary and GC analyses of some alkenyl- and alkinyl-cyanoacetates.

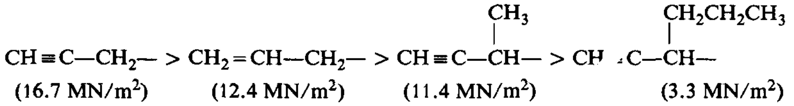
No.	Cyano-acetate	bp (°C/mmHg)	d_4^{20} (g/ml)	n_D^{20}	Calc. Found	C (%)	H (%)	N (%)	GC purity (%)	GC retn. time (s)
1	Allyl	115/19	1.0578	1.4426		57.60 57.5	5.60 5.6	11.20 11.5	100	355
2	Propargyl	113/13	1.1352	1.4557		58.54 58.7	4.06 4.0	11.38 11.2	100	537
3	2-Methyl-2-propenyl	81/6	1.0317	1.4487		60.43 60.2	6.47 6.3	10.07 10.3	100	466
4	2-Butenyl	96/10	1.0334	1.4510		60.43 60.3	6.47 6.5	10.07 10.0	98	450
5	1-Propyl-2-propenyl	135/14	—	1.4535		64.67 64.4	7.78 7.8	8.38 8.2	90	643
6	1-Methyl-2-propinyl	96/10	1.0775	1.4470		61.31 61.1	5.11 5.1	10.22 10.1	100	464
7	1-Propyl-2-propinyl	97/6	1.0228	1.4495		65.45 65.6	6.67 6.7	8.48 8.6	100	855

Tab. 2. Physical properties, elementary and GC analyses of some alkenyl- and alkinyl-2-cyanoacrylates.

No.	2-Cyanoacrylate	bp	n_D^{20}	Calc. Found	C	H	N	GC	
		(°C/ mmHg)	(g/ml)		(%)	(%)	(%)	purity (%)	retn. time (s)
1	Allyl	78/6	1.4600		61.31	5.11	10.22	100	205
					61.2	5.0	10.2		
2	Propargyl	68/2	1.4703		62.22	3.70	10.37	100	353
					62.4	3.8	10.2		
3	1-Methyl-2-propinyl	72/2	1.4623		64.43	4.70	9.40	100	259
					64.4	4.6	9.4		
4	1-Propyl-2-propinyl	80/2	1.4603		67.80	6.21	7.91	100	454
					67.9	7.2	8.0		

2-cyanoacrylate monomers. Their physical properties, elementary content and gas-chromatographic[4] purity are shown in Tab. 2. IR spectra confirmed the above mentioned monomers.

The alkenyl- and alkinyl-2-cyanoacrylates possess the typical adhesive properties of the alkyl-cyanoacrylate monomers, the set time being 10 to 60 s, while the maximum strength of the bond is achieved after 24 h. The studied cyanoacrylates may be ordered in the following sequence with respect to the shear tensile strength characteristics of steel-steel bonded joints:

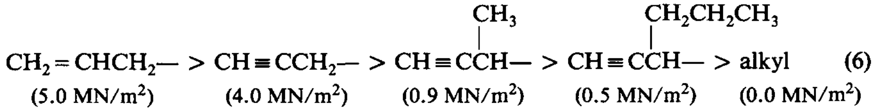


$$\underset{(16.7\ \mathrm{MN/m^2})}{CH{\equiv}C{-}CH_2{-}} > \underset{(12.4\ \mathrm{MN/m^2})}{CH_2{=}CH{-}CH_2{-}} > \underset{(11.4\ \mathrm{MN/m^2})}{CH{\equiv}C{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}} > \underset{(3.3\ \mathrm{MN/m^2})}{CH{\equiv}C{-}\overset{\overset{\displaystyle CH_2CH_2CH_3}{|}}{C}H{-}} \qquad (4)$$

The relationship is similar to that of the alkyl-2-cyanoacrylates, i. e. the bond strength depends primarily on the number of C atoms in the ester group of the molecule:

$$\begin{array}{cccccccccccc} \text{methyl} & > & \text{ethyl} & > & \text{propyl} & > & \text{butyl} & > & \text{hexyl} & > & \text{heptyl} \\ (18.0) & & (15.6) & & (9.3) & & (8.0) & & (3.1) & & (0.9) \end{array} \qquad (5)$$

The introduction of triple or double bonds into the ester group increases the tensile strength properties of the cyanoacrylate adhesives. On the other hand, if we try to correlate the thermal resistance of the adhesives, using the data for the tensile shear strength of steel-steel bonded joints treated for 24 h at 150 °C, we arrive at the following relationship:



$$\underset{(5.0\ \mathrm{MN/m^2})}{CH_2{=}CHCH_2{-}} > \underset{(4.0\ \mathrm{MN/m^2})}{CH{\equiv}CCH_2{-}} > \underset{(0.9\ \mathrm{MN/m^2})}{CH{\equiv}\overset{\overset{\displaystyle CH_3}{|}}{C}CH{-}} > \underset{(0.5\ \mathrm{MN/m^2})}{CH{\equiv}\overset{\overset{\displaystyle CH_2CH_2CH_3}{|}}{C}CH{-}} > \underset{(0.0\ \mathrm{MN/m^2})}{\text{alkyl}} \qquad (6)$$

Even the adhesive layer of unsaturated cyanoacrylate with 5 or 6 C atoms in the ester group had a better heat resistance than that of methyl- and ethyl-2-cyanoacrylates, whose bonds broke after treatment for 1 – 3 h at 150 °C. The best results were obtained with allyl-2-cyanoacrylate and propargyl-2-cyanoacrylate (Fig. 1 and 2).

The improved heat resistance of the alkenyl- and alkinyl-2-cyanoacrylates may be explained with the formation of cross-links in the adhesive layer. It can be seen in Fig. 1 that 24 h ageing at 100 °C doubled the tensile shear strength. Heating at this temperature for 7 days lead to an additional

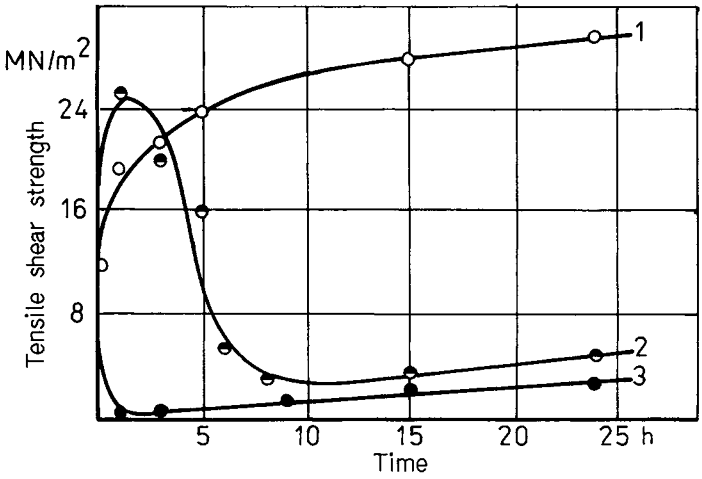


Fig. 1. Tensile shear strength as a function of thermal ageing of steel-steel bonded joints with allyl-2-cyanoacrylate.
(1 – 100 °C; 2 – 150 °C; 3 – 200 °C).

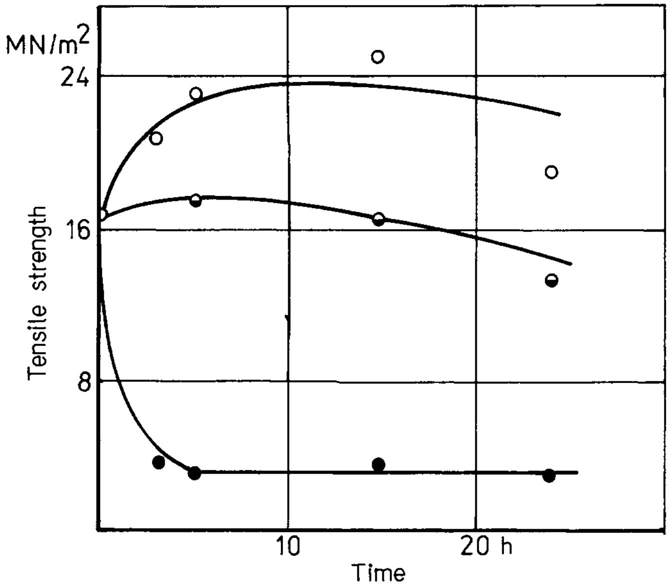


Fig. 2. Tensile strength as a function of thermal ageing of steel-steel bonded joints with propargyl-2-cyanoacrylate.
(○ – 100 °C; ⊖ – 150 °C; ● – 200 °C).

Tab. 3. Effect of the free-radical initiator on the tensile shear strength.

No.	Initiator	Quantity in monomer (%)	Tensile shear strength (MN/m^2)		
			Initial	After treatment for 3 h at 150 °C	
				tested hot	tested after cooling to 20 °C
1	None	—	12.4	9.4	20.0
2	Azobisisobutyronitrile	1.5	12.4	0.3	0
3	Azobisisobutyronitrile	3.0	17.1	4.1	2.5
4	Benzoylperoxide	3.0	15.5	2.2	0
5	Cumolhydroperoxide	1.5	13.6	4.4	5.5
6	Cumolhydroperoxide	3.0	11.9	3.8	5.5
7	Methylethylketone peroxide	1.5	11.4	2.4	3.6
8	Methylethylketone peroxide	3.0	12.4	3.1	3.6

increase of the strength characteristics. The deteriorating of properties at 150 °C and 200 °C may also be attributed to structural changes in the adhesive layer which cause internal strain and brittleness. An argument in favor of this assumption was the cohesive character of the bonds aged at 150 and 200 °C. Thermal degradation should also be included as a factor contributing to the loss of strength. Nevertheless, even after ageing at 200 °C the steel-steel bonded joints retain strength of more than 2 MN/m^2, which is satisfactory for most technical applications.

A logical way to promote cross-linking polymerization in the adhesive layer is to use free-radical initiators. We tried some common polymerization initiators (Tab. 3) and found that they have an adverse effect on the strength properties of allyl 2-cyanoacrylate bonded joints. This fact could be explained with the simultaneous formation of many active centers, leading to a denser network than the optimum one and to increased internal strains.

Some spectroscopic and thermogravimetric data may be cited as evidence of cross-linking reactions occurring in the polymers of the unsaturated cyanoacrylates. Qualitative IR measurements by the method of the base line[5] (Tab. 4) suggest a reaction of the double and triple bonds during the thermal treatment.

Tab. 4. IR absorbance changes of thermally treated poly(cyanoacrylates).

No.	2-Cyanoacrylate polymer	Wavenumber (cm^{-1})	Decrease of concentration of bond after 24 h treatment at 100 °C, (%)	Mass loss (%)
1	Allyl	$1655_{CH_2=CH-}$	10	0.3
2	Propargyl	$3340_{CH\equiv C-}$	19	1.0
3	1-Methyl-2-propinyl	$3330_{CH\equiv C-}$	17	1.8
4	1-Propyl-2-propinyl	$3340_{CH\equiv C-}$	16	4.0

Furthermore, by thermogravimetric studies we found that in the temperature range of depolymerization of cyanoacrylate polymers, the alkyl homologs had a typical endothermic peak, while the unsaturated homologs had an exothermic peak (Fig. 3). This means that, along with depolymerization and degradation, reactions of the double and triple bonds are occurring.

The thermal stability of the alkenyl and alkinyl 2-cyanoacrylate polymers (Tab. 5) confirms the above derived order (Eq. 6) for the heat resistance of their adhesive bonds.

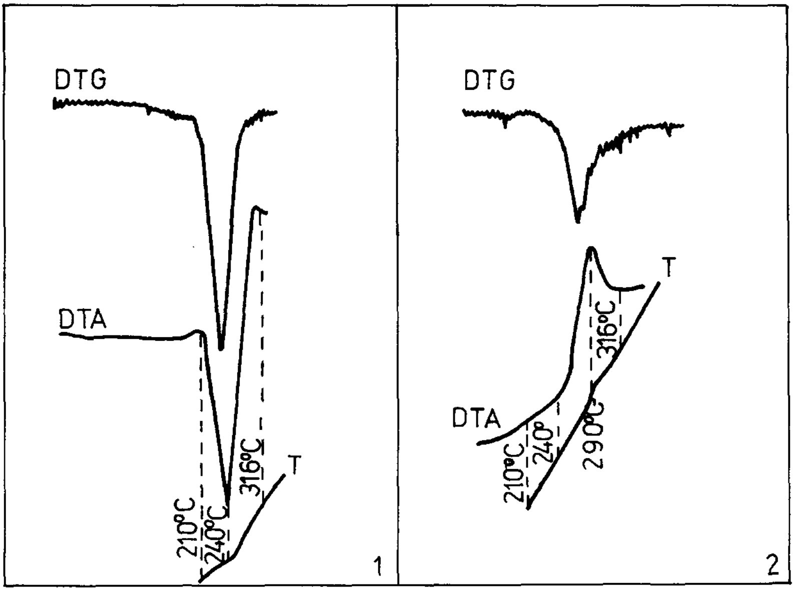


Fig. 3. Dynamic Thermogravimetry of poly(ethyl-2-cyanoacrylate) – (1) and poly(allyl-2-cyanoacrylate) – (2).

Experimental

The alkenyl- and alkinyl-cyanoacetates were obtained by direct esterification of cyanoacetic acid with the corresponding alcohols in the molar ratio 1.0 : 1.4 in the presence of 2% concentrated sulfuric acid, as catalyst and 100% toluene, for azeotropic removal of the reaction water. (The percentages are with respect to the cyanoacetic acid used.) After cooling, the reaction product was washed consecutively with 30% water solution of NaCl and 5% water solution of Na_2CO_3 until pH = 7 of the washing waters was achieved. The organic layer was then subjected to vacuum distillation and the cyanoacetate was isolated. For further purification it was rectified in vacuum.

Tab. 5. Thermal stability of some alkenyl- and alkinyl-2-cyanoacrylate polymers.

No.	Polymer	Thermal stability (°C)	
		10% mass loss	50% mass loss
1	Poly(allyl-2-cyanoacrylate)	215	395
2	Poly(propargyl-2-cyanoacrylate)	200	330
3	Poly(1-methyl-2-propinyl-2-cyanoacrylate)	195	263
4	Poly(1-propyl-2-propinyl-2-cyanoacrylate)	173	246

The alkenyl- and alkinyl-2-cyanoacrylates were obtained by a two step synthesis. The cyanoacetates were condensed with paraformaldehyde in the molar ratio 1 : 1 in the presence of 0.1% piperidine as catalyst and 100% toluene for azeotropic removal of water. The reaction product was then subjected to depolymerization in vacuum in a stream of SO_2. Prior to depolymerization, 1% P_2O_5 and 1% hydroquinone were added to the polymer. (All percentages are with respect to the cyanoacetate used.) The crude cyanoacrylate monomer was distilled again for purification.

The test specimens for determination of the tensile shear strength were steel made and had dimensions specified in DIN 53281/68. The tensile strength specimens were round, steel made, in compliance with ASTM-D-2094. Testing machine ZMGiT (DDR) was used with speed of extension 50 mm/min. The test specimens were not chemically treated. The adhesive was spread on a thin layer on one of the surfaces, against which the other surface was manually pressed for 60 sec. The surrounding air humidity and temperature were 55 – 65% and 20 – 22 °C. Testing of the adhered specimens were conducted 24 h after application of the adhesive. The thermal ageing was conducted in an oven at the given constant temperature. After treatment, the specimens were tempered in a desiccator to room temperature and subjected to testing. The graphical points are average values of 15 tested specimens.

IR measurements were made on a Specord 71 IR (DDR) with NaCl cells. Between the two plates of NaCl a thin layer of monomer was applied. It polymerized and the IR spectrum was surveyed 24 h after the application and after 24 h treatment at 100 °C.

The dynamic thermogravimetric analysis was carried out in a MOM (Hungary) derivatograph in a stream of N_2, with heating rate 2.5 °C/min. The analysed samples (~200 mg) for thermal stability were obtained by anionic polymerization of the corresponding monomers in water. The polymers were ground and dried to constant weight.

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