A Process for the Production of Biscyanoacrylates

This invention relates to a process for the production of biscyanoacrylates and to their use in cyanoacrylate adhesives.

Biscyanoacrylates and their production have been known for some time. They are produced by at least the following two methods:

- In the Knoevenagel condensation, formaldehyde is reacted with biscyanoacetates to form a crosslinked polymer which cannot readily be thermally depolymerized.
- In the Retro-Diels-Alder reaction, a monofunctional cyanoacrylate is first blocked with dienes. The blocked monofunctional cyanoacrylate is hydrolyzed to the free acid. The ester is then prepared from the corresponding acid chloride with a diol. Finally, after the biscyanoacrylate has been exchanged for maleic anhydride, the pure biscyanoacrylate is obtained after repeated recrystallization from benzene. Accordingly, this method of production comprises five stages and is thus uneconomical.

There is therefore a need for a simple method of producing pure biscyanoacrylate.

The solution provided by the invention is defined in the claims and essentially comprises transesterifying monocyanoacrylates with diols and working up the reaction mixture by fractional crystallization. The process according to the invention for the production of biscyanoacrylates is thus characterized in that 2-cyanoacrylic acid corresponding to the following general formula:

$$H_2C = C(CN)\text{-}CO\text{-}O\text{-}R^2 \qquad (II)$$

in which R^2 is a branched or unbranched alkyl group containing 1 to 6 carbon atoms,

or an alkyl ester thereof is transesterified with diols corresponding to the following general formula:

$$[HO]_2R^1 \qquad (III)$$

in which R^1 is a branched or unbranched difunctional alkane group containing 2 to 18 carbon atoms, which may also contain hetero atoms, such as halogens and oxygen, or aliphatic or aromatic rings,
to form biscyanoacrylates corresponding to the following general formula:

$$[H_2C = C(CN)\text{-}CO\text{-}O]_2R^1 \qquad (I)$$

and the reaction mixture is subsequently purified by fractional crystallization.

Accordingly, one starting product is the monofunctional cyanoacrylic acid corresponding to formula II or an alkyl ester thereof. The alkyl group should be selected so that the alcohol formed is easy to remove. Possibilities suitable for this purpose are known to the expert from the general transesterification reaction. The alcohol is preferably removed by distillation. R^2 is therefore a branched or unbranched alcohol radical containing 1 to 6 carbon atoms and preferably 1 or 2 carbon atoms. The monofunctional cyanoacrylate is stabilized in the usual way.

The diols are dihydric primary or secondary alcohols, preferably primary alcohols. The hydroxyl groups may be in any position to one another, although they are preferably in the α/ω position. The diols contain 2 to 18 carbon atoms and preferably 4 to 12 carbon atoms. They may be linear, branched or cyclic. The aliphatic radical may even be an aromatic group or,

in addition to the hydrogen and carbon atoms, may also contain hetero atoms, for example chlorine or oxygen atoms, preferably in the form of polyethylene or polypropylene glycol units. Suitable diols are hexanediol, octanediol, decanediol and dodecanediol.

The cyanoacrylate is used in excess. The molar ratio of monofunctional cyanoacrylate to diol is therefore at least 2.0:1.0, preferably 2.5:1.0 and more preferably 2.2:1.0.

The transesterification is catalyzed by strong acids, more especially by sulfonic acids, preferably by aromatic sulfonic acids such as, for example, p-toluene sulfonic acid. However, naphthalene sulfonic acid and benzene sulfonic acid and acidic ion exchangers may also be used as transesterification catalysts. The concentration of the transesterification catalyst should be between 1 and 20% by weight, based on the monofunctional cyanoacrylate.

The transesterification is carried out in solution as is normally the case. Suitable solvents are aromatic hydrocarbons and halogenated hydrocarbons. The preferred solvent is toluene or xylene. The concentration of the solution is in the range from 10 to 50% and preferably in the range from 10 to 20%.

The monohydric alcohol formed and the water formed are removed in known manner, preferably being distilled off with the solvent. The conversion of the transesterification reaction is monitored, for example with the aid of NMR spectra. The reaction takes several hours as usual. Where toluene is used as the solvent and p-toluene sulfonic acid as the catalyst, the reaction is over after 10 to 15 hours, i.e. no more alcohol separates off.

The working up of the reaction mixture is very important. Where acidic ion exchangers are used as the catalyst, they may simply be filtered off. Where soluble sulfonic acids, for example p-toluene sulfonic acid, are used as the catalyst, they are removed by solvent substitution, i.e. toluene is replaced by a mixture of hexane, heptane or decane. Pure biscyanoacrylate is obtained after two fractional crystallizations. According to NMR spectra,

the purity of the biscyanoacrylate exceeds 99%.

The biscyanoacrylate obtained is stable in storage with the usual stabilizers and in the usual concentrations, i.e. its melting point hardly changes after storage for 6 months at 20°C.

However, the biscyanoacrylates obtained polymerize very quickly in the presence of bases. As with monofunctional cyanoacrylates, traces of water are sufficient for this purpose. A three-dimensionally crosslinked polymer with relatively good thermal properties is formed.

Accordingly, it is preferably used in known cyanoacrylate adhesives in a quantity of 1 to 50% by weight and preferably in a quantity of 2 to 10% by weight, based on the adhesive as a whole.

Known cyanoacrylate adhesives contain as their principal component 2-cyanoacrylates corresponding to the following general formula:

$$H_2C = C(CN)\text{-}CO\text{-}O\text{-}R \qquad (IV)$$

in which R is an alkyl, alkenyl, cycloalkyl, aryl, alkoxyalkyl, aralkyl or haloalkyl group, more particularly a methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, hexyl, allyl, methallyl, crotyl, propargyl, cyclohexyl, benzyl, phenyl, cresyl, 2-chloroethyl, 3-chloropropyl, 2-chlorobutyl, trifluoroethyl, 2-methoxyethyl, 3-methoxybutyl and 2-ethoxyethyl group. The cyanoacrylates mentioned above are known to the expert on adhesives, cf. **Ullmann's Encyclopaedia of Industrial Chemistry, Vol. A1, page 240, Verlag Chemie, Weinheim (1985)** and **US-PS 3,254,111** and **PS-PS 3,654,340**. Preferred monomers are the allyl, methoxyethyl, ethoxyethyl, methyl, ethyl, propyl or butyl esters of 2-cyanoacrylic acid.

The adhesive may contain additives, for example plasticizers, thickeners, stabilizers, activators, dyes, etc.

The new cyanoacrylate adhesive according to the invention is particularly suitable for bonds which are expected to satisfy stringent thermal

requirements, for example for the bonding of electrical and electronic components.

The invention is illustrated by the following Examples.

I. Production of biscyanoacrylates

Using the general production process described in the foregoing, the starting products listed in Table 1 were reacted in 1 kg of toluene in the presence of p-toluene sulfonic acid as catalyst. The transesterification was over after 6 hours. The toluene was then replaced by hexane. The corresponding biscyanoacrylates with the melting points shown in the Table were obtained after two fractional crystallizations.

Table 1

No.	Starting Products	a) 1.0:0.5 Quantities in g	b) 1.2:0.4 Quantities in g	Melting Point °C
1.	Methyl cyanoacrylate	65.96	69.99	59-60
	Hexane-1,6-diol	35.05	27.68	
2.	Methyl cyanoacrylate	60.92	65.24	65-67
	Octane-1,8-diol	40.08	35.76	
3.	Methyl cyanoacrylate	56.63	61.10	74-75
	Decane-1,10-diol	44.38	39.91	
4.	Methyl cyanoacrylate	52.89	57.45	79-80
	Dodecane-1,12-diol	48.12	43.56	

II. Use of the biscyanoacrylates in cyanoacrylate adhesives

A few drops of the cyanoacrylate adhesive based on ethyl cyanoacrylate with the indicated additions of biscyanoacrylates were applied to the cleaned (blasted) aluminium or steel plates and cured for 24 hours at 20°C.

The bonded plates were then stored for 3 days at 20, 100 and 150°C and tested for strength at those temperatures.

Table 2 - Tensile Shear Strength (m N/mm²)

No.	Biscyanoacrylates		Substrate	Tensile shear strength		
	Type	Quantity [%]		20°C	100°C	150°C
1 a)	-	0	Steel		5	3
b)	-	0	Al		6	2
2	Hexanediol biscyanoacrylate	5	Steel	21	18	12
3	Octandiol	10	Al	18	16	10

CLAIMS

1. A process for the production of biscyanoacrylates corresponding to the following general formula:

$$[H_2C = C(CN)\text{-}CO\text{-}O]_2R^1 \qquad (I)$$

in which R^1 is a branched or unbranched difunctional alkane group containing 2 to 18 carbon atoms, which may also contain hetero atoms, such as halogen and oxygen, or aliphatic or aromatic rings,
characterized in that

a) 2-cyanoacrylic acid corresponding to the following general formula:

$$H_2C = C(CN)\text{-}CO\text{-}O\text{-}R^2 \qquad (II)$$

in which R^2 is a branched or unbranched alkyl group containing 1 to 6 carbon atoms,
or an alkyl ester thereof is transesterified with diols corresponding to the following general formula:

$$[HO]_2R^1 \qquad (III)$$

and

b) the reaction mixture is subsequently worked up by fractional crystallization.

2. A process as claimed in claim 1, characterized in that the transesterification is carried out in the presence of sulfonic acids, more particularly toluene sulfonic acid, in a concentration of 1 to 20% by weight, based on the monofunctional cyanoacrylate.

3. A process as claimed in claim 1 or 2, characterized in that toluene or xylene is used as the solvent for the transesterification and hexane, heptane

or decane is used for the fractional crystallization.

4. A storage-stable cyanoacrylate adhesive containing biscyanoacrylates corresponding to formula I, more particularly 1 to 50% by weight of biscyanoacrylates.

5. A cyanoacrylate adhesive as claimed in claim 4, characterized in that R^1 contains 6, 8, 10 or 12 carbon atoms.

6. A cyanoacrylate adhesive as claimed in claim 4 or 5 for bonding electrical and electronic components.