DICYANO ETHERS OF BISPHENOLS

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UDC 542.91+541.64+547.56

In the present paper we obtained and characterized some dicyano ethers of bisphenols of variable structure (Table 1), which were synthesized by the reaction of bisphenols with cyanogen chloride in the presence of triethylamine (see "Experimental" section). These compounds, the C ≡ N groups of which readily enter into the tricyclization reaction, are highly promising monomers for the synthesis of polymers – the polyarylcyanurates (PAC).

As the starting materials for the synthesis of the dicyano ethers we took bisphenols that contained various substituents attached to the central carbon atom: ranging from two protons to the cyclic anthrone grouping.

As the result of the induction effect of the substituents attached to the central carbon atom, or of the conjugation effect, the reactivity of the hydroxyl groups of bisphenols [1], and apparently also of the O – C ≡ N groups of the dicyano ethers, will depend on the structure of these compounds, which makes it possible to vary within wide limits both the synthesis conditions and the properties of the PAC prepared from them.

From the data given in Table 1 it can be seen that all of the dicyano ethers synthesized by us have narrow melting point ranges, and the calculated and found values of the elemental composition are in good agreement, which testifies to the purity of the obtained compounds.

Identification of the dicyano ethers of the bisphenols employing IR spectra disclosed the presence of strong absorption bands in the 1160-1235 cm^{-1} region, which are characteristic for the stretching vibrations of the C – O – C bond, and in the 2240-2285 cm^{-1} region, which belong to the stretching vibrations of the C ≡ N group of aromatic cyano ethers [2]. In this connection, in contrast to nitriles, the presence in this region of two or three absorption bands is characteristic for the C ≡ N group of the dicyano ethers of bisphenols.

In addition, in the IR spectra of the dicyano ethers is completely absent a very strong absorption band at 3200-3500 cm^{-1}, which belongs to the stretching vibrations of the OH group of bisphenols, which corroborates the quantitative conversion of the OH groups to O – C ≡ N groups during reaction.

As the result of a preliminary study of the polycyclotrimerization of the synthesized dicyano ethers of bisphenols we obtained some tough clear polymers with an initial deformation temperature $>400°C$, and an initial decomposition temperature of $\sim 400°$ when based on dynamic thermogravimetric analysis data.

The cast PAC also possess good physicomechanical indices. Thus, the polymer from 2,2-bis(4-cyanatophenyl)hexafluoropropane has a specific impact viscosity of 20 $\mathrm{kg \cdot cm/cm^2}$, a cross-breaking strength of 1200 $\mathrm{kg/cm^2}$, and a Brinell hardness of 1600 $\mathrm{kg/cm^2}$.

The PAC represent promising polymers for the fabrication of various materials with a high heat resistance.

EXPERIMENTAL

To a solution of 340.4 g of 9,9-bis(4-hydroxyphenyl)fluorene in 1000 ml of acetone, cooled to –10°, was added 129 g of liquid cyanogen chloride.

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TABLE 1. Properties of Dicyano Ethers of Bisphenols

No.	Dicyano ethers	Mp, °C	Found, %			Empirical formula	Calculated, %		
			C	H	N		C	H	N
1	$NCOC_6H_4—CH_2—C_6H_4OCN$	107,5—108	71,43 71,30	4,14 4,11	11,05 11,20	$C_{15}H_{10}N_2O_2$	71,99	4,02	11,19
2	$NCOC_6H_4—C(CH_3)_2—C_6H_4OCN$	81—82	73,57 73,68	5,06 5,02	9,88 9,89	$C_{17}H_{14}N_2O_2$	73,37	5,07	10,06
3	$NCOC_6H_4—C(CF_3)_2—C_6H_4OCN$	87,5—88,5	52,82 52,94	2,15 2,15	7,35 7,50	$C_{17}H_8F_6N_2O_2$	52,86	2,08	7,25
4	$NCOC_6H_4—C(H)(C_6H_5)—C_6H_4OCN$	72,5—73	77,09 77,04	4,37 4,08	8,53 8,76	$C_{21}H_{14}N_2O_2$	77,28	4,32	8,58
5	$NCOC_6H_4—C(CH_3)(C_6H_5)—C_6H_4OCN$	87—88	77,71 77,82	4,72 4,57	8,18 8,38	$C_{22}H_{16}N_2O_2$	77,64	4,73	8,23
6	$NCOC_6H_4—C(C_6H_5)_2—C_6H_4OCN$	190,5—191,5	80,73 80,51	4,51 4,73	6,92 7,07	$C_{27}H_{18}N_2O_2$	80,59	4,47	6,96
7	3,3-Bis(4-cyanatophenyl)phthalide	134—135	72,02 71,81	3,59 3,43	7,60 7,40	$C_{22}H_{12}N_2O_4$	71,73	3,29	7,60
8	9,9-Bis (4-cyanatophenyl) fluorene	162,5—163	81,06 81,00	4,05 4,05	7,08 7,09	$C_{27}H_{16}N_2O_2$	80,98	4,03	7,00
9	9,9-Bis(4-cyanatophenyl)-10-anthrone	169—170	78,21 78,63	3,90 3,89	6,24 6,06	$C_{28}H_{16}N_2O_3$	78,50	3,76	6,54
10	p—$NCOC_6H_4OCN$	115—116	60,15 60,24	2,74 2,65	17,30 17,13	$C_8H_4N_2O_2$	60,01	2,52	17,49
11	m—$NCOC_6H_4OCN$	78—79,5	59,86 59,71	2,30 2,21	17,61 17,67	$C_8H_4N_2O_2$	60,01	2,52	17,49

With cooling (0-3°) and good stirring, to the reaction mixture was added 206 g of triethylamine in drops. A precipitate of triethylamine hydrochloride was formed. The reaction mixture was stirred for another 10-15 min, and the flask contents were poured into 5 liters of ice water. The obtained 9,9-bis(4-cyanatophenyl)fluorene was filtered, washed with ice water until neutral, and dried in vacuo at 20°. Yield 380 g (95% of theory); mp 158°.

The dicyano ethers of the other bisphenols were synthesized in a similar manner.

The obtained products were purified by recrystallization from such solvents as petroleum ether, heptane, octane, and also mixtures of toluene with these solvents. The melting points of the twice recrystallized dicyano ethers are given in Table 1.

CONCLUSIONS

Some dicyano ethers of bisphenols of variable structure were synthesized and their properties were studied. It was shown that the dicyano ethers can be used as monomers for the preparation of heat-resistant polymers, namely polyarylcyanurates.

LITERATURE CITED

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