Viscosity of the Homologous Series of *n*-Alkylcyanobiphenyls

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The paper presents the shear viscosity data for the isotropic phase of the homologous series of mesogenic *n*-alkylcyanobiphenyls ($C_nH_{2n+1}PhPhC{\equiv}N$, *n*CB) for $n = 2-12$.

Introduction

In a recent paper[1] we presented the results of the shear viscosity measurements performed for the homologous series of 4-(*trans*-4′-*n*-alkylcyclohexyl)isothiocyanatobenzenes ($C_nH_{2n+1}CyHxPhN{=}C{=}S$, $n = 0-12$). The molecules of this series are of moderate polarity:[2] the dipole moment of a single molecule is about 3.5 D. For $n \geq 2$ the compounds are nematogenic; that is, in the temperature range below the characteristic value T_{ni}, they are the nematic liquid crystals. Because the viscosity of the nematics is an anisotropic quantity, the conventional methods of measurement, such as with a rotator viscometer, have only limited applications.[3] So, the measurements were made on the isotropic phase of the liquids only.

This paper presents the shear viscosity data for the most popular liquid crystalline homologous series—*n*-alkylcyanobiphenyls ($C_nH_{2n+1}PhPhC{\equiv}N$, $n = 2-12$) composed of the strong polar molecules ($\mu \approx 5$ D).[2] The series presents a great variety of mesogenic ability: from the nematogenic ($3 \leq n \leq 7$), through both nemato- and smectogenic ($n = 8$ and 9), to only smectogenic ($n \geq 10$) compounds. The temperatures of the phase transitions are presented in Table 1. As with the 4-(*trans*-4′-*n*-alkylcyclohexyl)isothiocyanatobenzenes, the results presented here are only for the isotropic phase.

Experimental Section

The *n*-alkylcyanobiphenyls were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compounds, determined with the chromatographic method, was 99.5 mass % as a standard, with an exception of the $n = 8$, 9, and 10 members of the series, which were of higher purity (99.9 mass %).

The shear viscosity was measured with a Haake viscometer Rotovisco RV 20 with the measuring system CV 100. The shear rate (velocity gradient) was 275 s^{-1}. In the available range of the shear rates (30 s^{-1} to 300 s^{-1}) the studied compounds show Newtonian behavior; that is, the value of the viscosity does not depend on the velocity gradient. Figure 1 presents, as an example, the Newtonian behavior of *n*-heptylcyanobiphenyl at 323 K.

The accuracy of the viscosity determination was about ±1%.

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Table 1. Values of the Phase Transition Temperature for the *n*-Alkylcyanobiphenyl Homologous Series[a]

n	T_m/K	$T_{n,i}$/K	$T_{n,sa}$/K	$T_{sa,i}$/K
2	348.0			
3	339.0	(298.5)[b]		
4	321.0	(289.5)		
5	297.0	308.3		
6	287.5	302.0		
7	303.0	315.8		
8	294.5	313.5	306.5	
9	315.0	322.5	321.0	
10	317.0			323.5
11	326.0			330.5
12	321.0			331.5

[a] The symbols i, n, and sa denote the isotropic, nematic, and smectic A phases, respectively; *n* is the number of carbon atoms in the alkyl chain of the molecule. [b] The parentheses denote the monotropic phase transition.

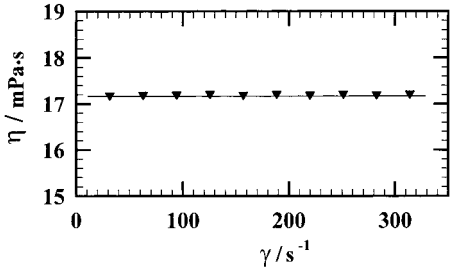

Figure 1. Newtonian behavior of *n*-heptylcyanobiphenyl in the isotropic phase at 323 K.

Results and Discussion

The results of the viscosity measurements for *n*-alkylcyanobiphenyls are presented in Table 2 and Figure 2. The solid lines in the figure correspond to the best fitting of the Vogel−Tamman−Fulcher (VTF) equation:[4,5]

$$\eta(T) = \eta_\infty \exp\left[\frac{DT_0}{T - T_0}\right] \tag{1}$$

to the experimental values of the viscosity. The values of the fit parameters η_∞, D, and T_0 are given in Table 3. The table contains also the standard deviation calculated with the following equation:

$$\sigma = \left(\frac{\sum_i (\eta_{exp} - \eta_{calc})^2}{n_d - n_p}\right)^{1/2} \tag{2}$$

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Table 2. Experimental Values of the Shear Viscosity η of the Homologous Series of *n*-Alkylcyanobiphenyls in the Isotropic Phase

T/K	η/mPa·s	T/K	η/mPa·s	T/K	η/mPa·s
			$n = 2$		
341.4	5.41	348.0	4.62	354.6	4.03
342.3	5.24	348.9	4.53	355.5	3.95
343.2	5.16	349.9	4.44	356.4	3.87
344.2	5.07	350.8	4.37	357.4	3.76
345.2	4.96	351.7	4.27	358.3	3.70
346.1	4.88	352.7	4.18	359.3	3.62
347.0	4.72	353.6	4.08		
			$n = 3$		
317.9	14.47	334.8	7.98	345.2	5.99
319.8	13.49	335.8	7.70	346.1	5.84
321.6	12.56	336.7	7.53	347.0	5.70
323.5	11.65	337.6	7.34	348.0	5.54
325.4	10.85	338.6	7.18	348.9	5.44
327.3	10.16	339.5	6.93	349.9	5.33
329.2	9.58	340.5	6.81	351.7	5.05
331.0	8.92	341.4	6.61	353.6	4.79
332.0	8.65	342.3	6.51	355.5	4.63
332.9	8.41	343.3	6.27	357.4	4.42
333.9	8.22	344.2	6.13	359.3	4.19
			$n = 4$		
301.9	30.41	322.6	12.78	342.3	6.97
304.7	26.49	325.4	11.61	345.2	6.43
307.5	23.43	328.2	10.53	348.0	5.99
310.4	20.73	331.0	9.60	350.8	5.55
313.2	18.30	333.9	8.74	353.6	5.25
316.9	15.76	336.7	8.10	356.4	4.91
319.8	14.17	339.5	7.52	359.3	4.65
			$n = 5$		
308.5	25.78	321.6	15.15	340.5	8.23
310.4	23.80	323.5	14.21	345.2	7.28
312.2	22.01	325.4	13.26	349.9	6.53
314.1	20.37	327.3	12.42	354.6	5.84
316.0	18.89	329.2	11.65	359.3	5.28
317.9	17.48	331.0	11.00		
319.8	16.20	335.8	9.47		
			$n = 6$		
306.3	32.12	317.6	19.82	340.2	9.10
308.2	29.50	319.5	18.44	344.9	8.06
310.1	27.13	321.3	17.12	349.6	7.14
311.9	24.99	326.0	14.41	354.3	6.39
313.8	23.10	330.7	12.26	359.0	5.69
315.7	21.40	335.5	10.56		
			$n = 7$		
317.2	20.59	325.7	14.95	340.8	9.28
318.2	19.78	327.6	14.01	345.5	8.08
320.1	18.45	329.5	13.28	350.2	7.21
321.9	17.22	331.3	12.41	354.9	6.39
323.8	16.09	336.1	10.67	359.6	5.76
			$n = 8$		
314.1	25.84	325.4	16.78	345.2	9.03
316.0	23.97	327.3	15.66	349.9	8.03
317.9	22.20	329.2	14.70	354.6	7.18
319.8	20.70	331.0	13.82	359.3	6.41
321.6	19.33	335.8	11.87		
323.5	17.97	340.5	10.30		
			$n = 9$		
323.0	19.64	325.4	17.95	340.5	11.01
323.1	19.48	326.3	17.39	345.2	9.64
323.3	19.35	327.3	16.76	349.9	8.49
323.5	19.28	329.2	15.74	354.6	7.57
324.0	18.88	331.0	14.75	359.3	6.85
324.5	18.61	335.8	12.79		
			$n = 10$		
332.9	14.94	344.2	10.68	355.5	7.91
336.7	13.31	348.0	9.63	359.3	7.16
340.5	11.95	351.7	8.65		
			$n = 11$		
332.9	16.43	344.2	11.52	355.5	8.56
336.7	14.56	348.0	10.35	359.3	7.84
340.5	13.04	351.7	9.29		
			$n = 12$		
332.9	17.52	344.2	12.36	355.5	9.01
336.7	15.45	348.0	11.05	359.3	8.23
340.5	13.81	351.7	10.05		

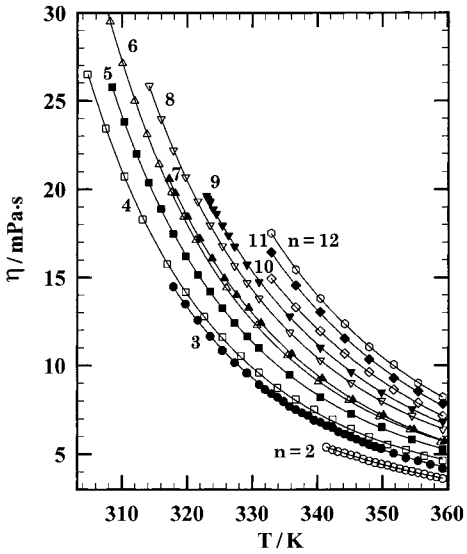

Figure 2. Temperature dependence of the shear viscosity of *n*-alkylcyanobiphenyls. *n* denotes the number of carbon atoms in the alkyl chain of the molecule. The solid lines represent the best fitting of eq 1 to the experimental values of the viscosity.

Table 3. Values of the Parameters η_∞, D, and T_0 Corresponding to the Best Fitting of Eq 1 to the Viscosity Experimental Data for *n*-Alkylcyanobiphenyls

n	η_∞/mPa·s	D	T_0/K	σ^a/mPa·s
2	0.0107	20.8486	78.464	0.021
3	0.1328	2.7359	200.753	0.044
4	0.1216	3.1858	191.493	0.067
5	0.1654	2.8017	198.501	0.061
6	0.1204	3.4562	189.302	0.076
7	0.1074	3.7372	185.403	0.047
8	0.1458	3.3003	191.902	0.055
9	0.1730	3.0267	196.978	0.047
10	0.0133	14.6860	107.721	0.040
11	0.2710	2.2658	214.599	0.096
12	0.0437	7.2939	150.156	0.039

[a] σ denotes the standard deviation (eq 2).

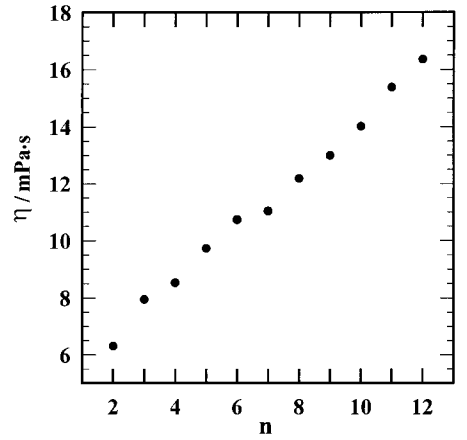

Figure 3. *n* dependence of the viscosity of the *n*-alkylcyanobiphenyls at $T = 345$ K.

where n_d and n_p denote the number of experimental points and the number of parameters, respectively.

The VTF equation, which primarily was used for reproduction of the $\eta(T)$ dependences of supercooled liquids,[4,5] appears to be also suitable for the empirical description of the temperature dependence of the viscosities of the mesogenic liquids in the isotropic phase.

It is worthwhile to notice that the standard deviation corresponding to the best fitting of the Arrhenius equation

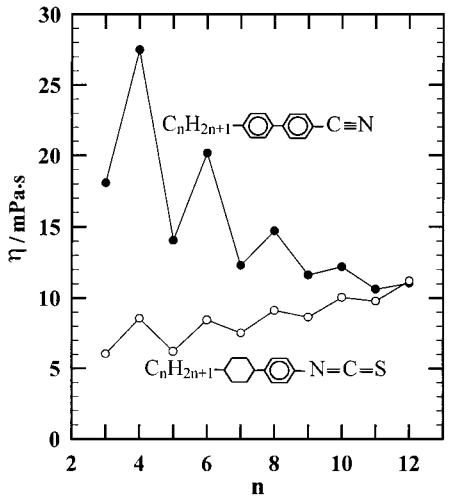

Figure 4. Odd−even effect in the *n* dependence of the viscosity of *n*-alkylcyanobiphenyls (●) and 4-(*trans*-4-*n*-alkylcyclohexyl)-isothiocyanatobenzenes (○) at constant reduced temperature $T^* = 1.05$.

to the presented viscosity data is 1 order of magnitude higher than that corresponding to the VTF equation (Table 2). In the case of the homologous series of 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes, the standard deviations corresponding to both equations are of the same order of magnitude.

Figure 3 presents the isothermal viscosity dependence on the number of carbon atoms (*n*) in the alkyl chain of *n*-alkylcyanobiphenyl molecules. As expected, the viscosity monotonically increases with *n*. A similar dependence was observed for 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes.[1] However, at constant reduced temperature T^* ($=T/T_c$, T_c is the temperature of transition from isotropic to nematic (or to smectic for $n = 10-12$) phase, see Table 1) the *n* dependences of the viscosities of both homologous series are different (Figure 4). The evolution of the odd−even effect, due to an increase of the alkyl chain length, leads to a decrease of the viscosity in the case of *n*-alkylcyanobiphenyls and to an increase of the viscosity in the case of 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes. The equality of the viscosities for $n = 12$ in both series is rather by chance.

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