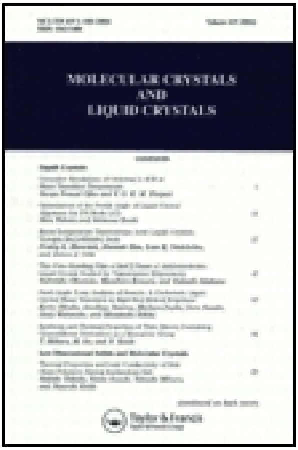

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LIQUID CRYSTALLINE COMB-SHAPED POLY(VINYL ETHER)S WITH CYANBIPHENYL MESOGENIC GROUPS

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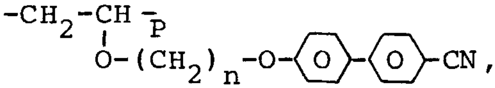
Abstract The synthesis of the series of new liquid crystalline comb-shaped poly(vinyl ether)s with cyanbiphenyl mesogenic groups is reported. Methylenic spacer groups of the different lengths (n=2-6,11) were used. Polymers were prepared by cationic polymerization corresponding vinyl ethers. The influence of molar mass and molar mass distribution on the mesomorphic properties and phase transitions has been studied. The effect of chemical structure of the main chain on the mesomorphic properties is discussed.

INTRODUCTION

At present it is well established that the chemical nature and flexibility of the main chain of comb-shaped liquid crystalline (LC) polymers essentially influence on mesophase type and its thermodynamical properties. Although increase of the main chain flexibility results in the regular glass transition (T_g) shift towards lower temperatures, the change of clearing temperature (T_{cl}) and mesophase types are often unpredictable[1]. The role of the main chain flexibility in the formation of LC state of comb-shaped polymers and its effect on mesophase type and T_{cl} cannot be considered as completely elucidated; it needs the comparative investigations of the different homologous series of comb-shaped polymers with an identical mesogenic groups.

The first goal of this paper is to obtain the new homologous series of LC poly(vinyl ether)s (I) with high polar cyanbiphenyl mesogenic groups and aliphatic spacers of the different length[*] as well as to discuss some regularities and relationships between their molecular parameters (molar mass and molar mass distribution) and the phase transitions.

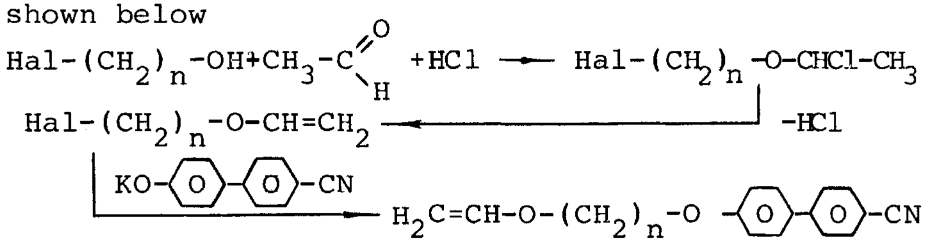


where n=2-6,11 (I)

The second goal is to compare briefly the thermal properties of the synthesized **LC** poly(vinyl ether)s with the ones of LC polyacrylates, methamethacrylates and polysiloxanes with the same mesogenic groups[4-6].

MONOMER SYNTHESIS AND PROPERTIES OF MONOMERS

Monomers were synthesized according to the scheme shown below



n = 2-6,11 Hal = Cl, Br

The mesogenic behaviour of the monomers and polymers was investigated by a "Polam" polarizing microscope equipped with a "Mettler FP-800" hot stage.

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[*] Some of LC comb-shaped poly(vinyl ether)s were recently synthesized and described by Percec[2] and Lenz[3] et al.

The properties of the synthesized monomers are listed in Table 1.

TABLE 1. Phase Behaviour of Monomers
$CH_2=CH-O-(CH_2)_n-O-C_6H_4-C_6H_4-CN$

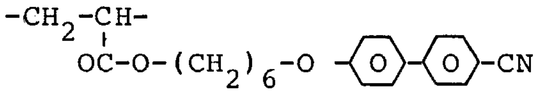
n	Phase and Phase Transitions, °C
2	K 116 I
3	K 61 I
4	K 71 N 77 I
5	K 48 (N 41) I
6	K 70 N 75 I
11	K 68 (N 56) I

The existence of oxyvinyl group in the monomer molecules leads to the strong alternation of melting points and clearing temperatures of vinylethers under investigation. We can note in Table 1 that the stability of the mesophase for monomers with an even number of CH_2-groups (n=4 and 6) is comparable with one of corresponding homologues of alkoxycyanbiphenyls (n-OCB)[7]. However the temperature interval of mesophase is slightly narrow as compared with one of n-OCB series owing to more high values of T_m. At the same time the homologue with n=5 forms only monotropic LC phase and has more low values T_{cl} as compared to monomers with n=4 and 6.

POLYMER SYNTHESIS AND PROPERTIES OF POLYMERS

The polymers were prepared by cationic polymerization using J_2 and $BF_3 \cdot O(C_2H_5)_2$ as initiators[8]. The reactions were carried out in Schlenk tube under dry argon atmosphere. The polymers were precipitated with cold ammoniacal methanol. The products were dissolved in methylene chloride and twice reprecipitated with methanol. The polymers were dried in a vacuum. The reaction conditions and some characteristics of the polymers are summarized in Table 2.

The average molar mass and molar mass distribution of the synthesized polymers were measured by GPC ("Waters GPC-2 equipped with three styragel columns, differential refractometric detector). The tetrahydrofuran solutions with concentration of polymers lower 1% (weight) were used for chromatography. As the calibration standards the fractions of polymer II with well-known values of molar mass lying in interval $M_n=6,15\cdot10^3-1\cdot10^5$ and polydispersity, $M_w/M_n= 1.15-1.39$ (independently determined by GPC and light scattering) were used



$$\begin{array}{l} -CH_2-CH- \\ \qquad\quad | \\ \qquad OC-O-(CH_2)_6-O-C_6H_4-C_6H_4-CN \end{array}$$

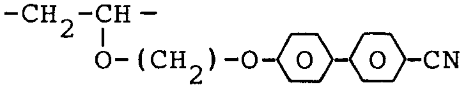
(II)

As it has been recently shown[9] as well as it has been established by us in preliminary experiments the application of polystyrene standards for determination of molar mass parameters of LC polymers by GPC has led to essential errors. That is why we have chosen the polymer II as a standard whose molecular structure is very similar to the one of polymers of series (I). Table 3 presents the results of GPC of some of synthesized polymers.

RESULTS AND DISCUSSION

The comparison of data presented in Table 2 and 3 shows that the usage of the different initiator

TABLE 2. Reaction conditions*, yields, intrinsic viscosity and phase transitions of the polymers



Polymers	n	Yield, %	[η]**, dl/g	Phases and Phase Transitions, °C
		Initiator J_2/(1 mM); T = -15°C		
2.1	2	50	-	no mesophase
3.1	3	30	-	N 94° I
4.1	4	55	0.050	N 78° I
5.1	5	60	0.060	S_A 91 N 108 I
6.1	6	57	-	S_A 90 N 103 I
6.1a	(fraction)	-	0.072	S_C 54 S_A 116 I
6.1b	-"-	-	0.062	S_C 45 S_A 116 I
6.1c	-"-	-	0.050	S_A 97 N 103 I
11.1	11	48	-	S_A 104-145 I
11.1a	(fraction)	-	0.070	S_A 133-145 I
11.1b	-"-	-	0.060	S_A 114-140 I
11.1c	-"-	-	0.055	S_A 108-140 I
		Initiator $BF_3 \cdot O(C_2H_5)_2$ (20 mM) T= -70°C		
2.2	2	80	0.056	no mesophase
3.2	3	50	0.040	N 78 I
4.2	4	50	0.060	N 73 I
4.2a	(fraction)	-	0.065	N 74 I
4.2b	-"-	-	0.060	N 69 I
4.2c	-"-	-	0.055	N 62 I
5.2	5	55	0.054	S_A 65 N 98 I
6.2	6	40	0.060	S_A 98 N 100 I
6.2a	(fraction)	-	0.070	S_C 38 S_A 110 I
6.2b	-"-	-	0.060	S_C 33 S_A 107 I
6.2c	-"-	-	0.055	S_A 90-96 I
11.2	11	30	0.065	S_A 100-107 I

* Monomer concentration 0.36 M, solvent - CH_2Cl_2 Polymerization time - 60 min.

** 1,2 Dichloroethane, 30°C.

TABLE 3. Molecular characteristics of some synthesized poly(vinyl ether)s

Polymer	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w/M_n	$P_n (P_w)$
5.1	5.32	9.16	1.72	17 (30)
5.2	3.44	5.88	1.71	11 (19)
6.1a	6.40	8.73	1.36	20 (27)
6.1b	5.12	6.26	1.22	16 (20)
6.1c	2.84	3.58	1.26	9 (11)
6.2	4.12	7.25	1.76	13 (23)
6.2a	4.80	7.31	1.52	15 (23)
6.2b	4.61	7.13	1.55	14 (22)
6.2c	3.77	5.84	1.55	12 (18)

systems leads to the similar results. In both the cases only oligomer compounds with close molar mass distribution (M_w/M_n=1,7-1,8) are formed. The fractionation of synthesized polymers by fractional precipitation (Table 3, polymers 6.1,a-c/6.2, a-c) permits to decrease the polydispersity to a certain degree. Low molar mass of the polymers affect their mesomorphic behaviour, as it is observed for LC polyacrylates[10] with low degree of polymerization (DP). So the increase of DP for polymer fractions 6.1,a-c (Table 3) results in increasing of the clearing temperature and variation of mesophase types. The lowest molar mass fraction of polymer 6.1 (P_n=9) is characterized by S_A and N-phases; fraction 6.1,b (P_n=16) gives S_A and tilted S_C phases. It is important to note that all these fractions possess sufficiently narrow molar mass distribution. At the same time the more wide molar mass distribution of unfractionated polymers 6.1 and 6.2.(Table 3) leads to decreasing clearing temperatures. Most likely the more wide molar mass distribution of polymer fractions 6.2,a-c (Table 3), obtained by using initiator systems $BF_3 \cdot O(C_2H_5)_2$ predetermines their lower clearing temperatures as comparison with polymer fractions 6.1,a-c (Table 3) synthesized using J_2 as an initiator. All these data clearly shows the effect of molar mass distribution width on phase transitions and mesophase types.

Considering the phase behaviour of all the synthesized polymers it is necessary to note the influence of the spacer length on the mesophase types. For example the polymers with very short spacer length (n=2) do not display LC properties; the increase of the spacer length (n=3,4) leads to nematic mesophase and further increase of it (n>5) gives smectic mesophases. Thus the character of the variation of mesophase types in polyvinylethers looks like the situation in the homologous series of low molar mass liquid crystals - alkoxycyanbiphenyls; however the behaviour of poly(vinyl ether)s is considerably different from the one of polymer liquid crystals having polymethacrylic, polysiloxane main chains (S_A phase is characteristic for n=4-6,11)[4,5] and polyacrylic backbone (N phase for n=2,4,6; S_A phase for n=3,5,11)[6].

Analogy of mesomorphic behaviour of poly(vinyl ether)s under investigation and low molar mass liquid crystals are most likely conditioned by the "simplicity" of polyether's main chain structure (relatively small volume of monomeric unit, absence of strong dipoles) and its minimum influence on the side chain packing.

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