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Synthesis of several series of liquid crystalline polyaroyl-bis-oxyarylates and their structure–property relationships

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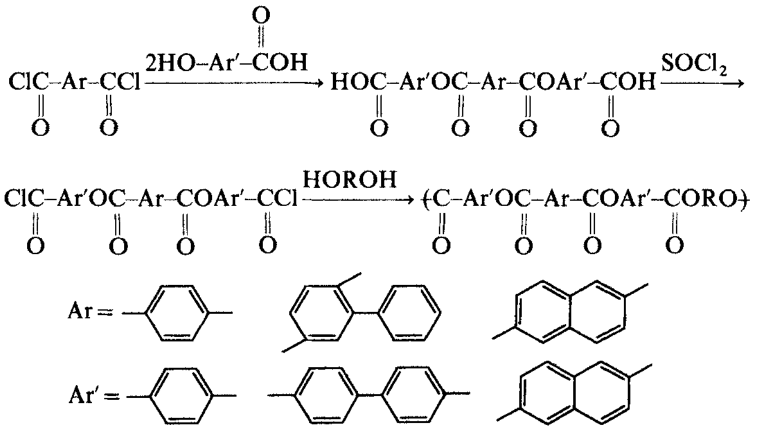
Several series of liquid crystalline polyaroyl-bis-oxyarylates containing 1,4-phenylene, 4,4′-biphenylene and 2,6-naphthylene units have been synthesized with the use of aroyl-bis-oxyaroyl dichlorides. Melting and clearing temperatures of every polymer under investigation were compared with those of corresponding polyterephthaloyl-bis-4-oxybenzoates.

1. Introduction

Investigation of structure–property relationships is of high importance for both low molecular weight and polymer liquid crystals. 1,4-Phenylene, 4,4′-biphenylene, 2,5-biphenylene, 2,6-naphthylene and *trans*-1,4-cyclohexylene are the main structural units used in the molecular design of liquid crystals (LC) polymers. The present work deals with the determination of the relative contribution of various single structural units in LC polymers, thermal properties and mesogenic capability. It is evident that in order to understand these contributions correctly we need a number of well-characterized LC substances with regular variations in their structure.

2. Polymer synthesis

Two approaches to the synthesis of main chain LC polymers have been developed by authors during the last decade. The first one consists of the synthesis of a 'complex' monomer, whose structure corresponds to that of the mesogenic group. Subsequent polycondensation of this monomer with a single or another complex gives us LC polymers with a regular structure [1]. A number of complex acid dichlorides containing various single structural units have been synthesized, characterized and used in LC polymer synthesis [2, 3] (see scheme 1).



$$\underset{\underset{\mathrm{O}}{\|}}{\mathrm{ClC}}\mathrm{-Ar-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{CCl}}\xrightarrow{\mathrm{2HO-Ar'-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{HOC}}\mathrm{-Ar'O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{-Ar-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OAr'-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH}\xrightarrow{\mathrm{SOCl_2}}$$

$$\underset{\underset{\mathrm{O}}{\|}}{\mathrm{ClC}}\mathrm{-Ar'O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{-Ar-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OAr'-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Cl}\xrightarrow{\mathrm{HOROH}}\mathrm{\{}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{-Ar'O}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{-Ar-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OAr'-}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{ORO\}}$$

Scheme 1. Synthesis of LC polymers via mesogenic acid dichlorides.

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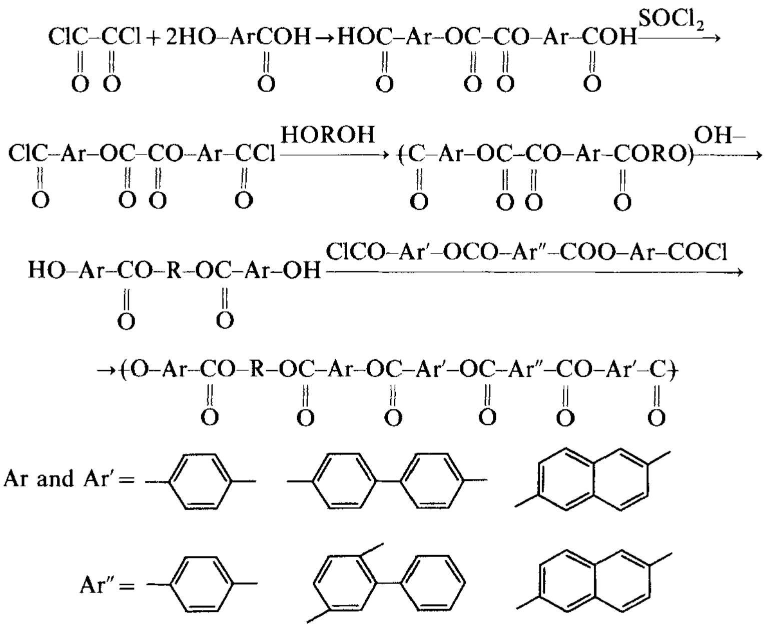
The second approach enables us to synthesize LC polymers with increased length of the mesogenic group [4]. These polymers may be considered as multiblock copolymers with a rigid, mesogenic block of exactly definite length and chemical structure. This approach consists of the synthesis of bis-hydroxyaroyl derivatives of polyethylene and polypropylene glycols or any other dihydroxyl compounds through selective hydrolysis of the intermediate polymer. Polycondensation of these derivatives with triad type mesogenic acid dichlorides gives the desired polymers (see scheme 2).



Scheme 2. Synthesis of LC polymers with an increased length of the mesogenic group.

Several series of LC polymers based on decamethylene, diethylene (DiEG), triethylene (TriEG), tetraethylene (TetraEG), hexaethylene (HexaEG) glycols and various triad-type mesogenic acid dichlorides have been synthesized in a high temperature solution polycondensation procedure [1]. In addition some LC polymers containing five single structural units in the mesogenic group have been synthesized based on polyethylene glycol-1000.

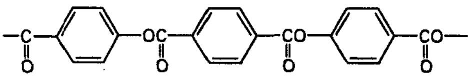
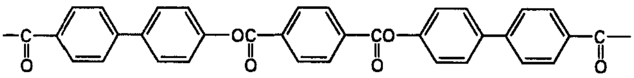
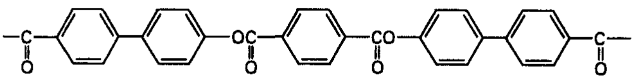
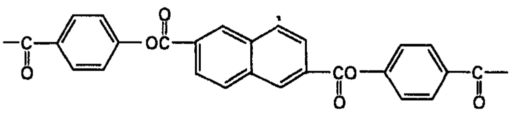
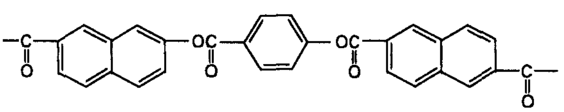
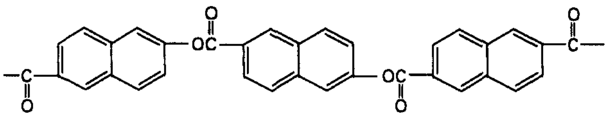
The synthesized polymers were characterized by viscometry, elemental analysis, spectral methods, polarizing optical microscopy and differential scanning calorimetry. Only melting and clearing temperatures of the polymers determined by the latter two methods are of interest in this work.

The chemical structures of the triad-type LC polymers are given in table 1. Some properties of the triad type polymers are given in table 2. Viscosity values were measured in CF_3COOH/CHl_3 mixture (3:2) at 25°C.

3. Analysis of the phase transition temperatures of polymers I–VI

The phase transition temperatures of the polymers were determined by differential scanning calorimetry when possible. Polarizing optical microscopy data were used when no or several peaks were found on DSC curves. A difference between DSC and microscopy data was generally very small.

Table 1. Chemical structures of the triad-type LC polymers.

Structure of polymer mesogens	Designation and number of series	
	T-OB	I
	T-OBP	II
	PT-OBP	III
	N-OB	IV
	T-ON	V
	N-ON	VI

Spacers: $-O(CH_2)_{10}-O-$; diethylene, triethylene, tetraethylene and hexaethylene glycols.

The polymers form mainly smectic-type mesophases whose order decreases with decreasing symmetry of the mesogenic group. The structure of the polymer melts is under detailed investigation at present and the results will be reported elsewhere.

When measuring clearing temperatures we must take into consideration that some chemical transformations distort the chemical structures of the polymers at temperatures above 300 C. Transesterification may be one such reaction.

In order to avoid the strong influence of thermal, chemical transformations on the clearing temperatures, the temperatures were measured with a high heating rate, by placing the samples on a preheated heating stage. Thermochemical transformations did not occur during the short measuring time, such that the real clearing temperatures were not altered significantly.

Direct comparison of the melting and clearing temperatures of polymers of various series was rather complicated and not very informative. In order to obtain some semi-quantitative parameter to compare LC polymers with different single structural units we have reduced the melting and clearing temperatures of every polymer under

Table 2. Intrinsic viscosities, melting and clearing temperatures of the polymers I–VI.

Mesogen	Spacer	$[\eta]/\mathrm{dl\,g^{-1}}$	T_M/K	T_C/K
T-OB (series I)	$(CH_2)_{10}$	2·90	496	571
	Di-EG	0·60	474	622
	Tri-EG	1·00	469	569
	Tetra-EG	0·80	413	508
	Hexa-EG	0·70	388	416
T-OBP (series II)	$(CH_2)_{10}$	Insol.	603	Above T_d
	Di-EG	—	573	—
	Tri-EG	0·40	550	—
	Tetra-EG	0·55	515	—
	Hexa-EG	1·40	485	630
PT-OBP (series III)	$(CH_2)_{10}$	0·70	495	606
	Di-EG	0·80	467	600
	Tri-EG	1·15	398	523
	Tetra-EG	0·50	355	473
	Hexa-EG	0·50	322	405
N-OB (series IV)	$(CH_2)_{10}$	0·70	495	606
	Di-EG	0·40	485	615
	Tri-EG	0·40	487	583
	Tetra-EG	0·41	423	546
	Hexa-EG	0·52	408	478
T-ON (series V)	$(CH_2)_{10}$	1·23	490	Above T_d
	Di-EG	Insol.	453	—
	Tri-EG	0·40	455	—
	Tetra-EG	0·60	383	583
	Hexa-EG	0·45	365	485
N-ON (series VI)	$(CH_2)_{10}$	1·00	540	Above T_d
	Di-EG	Insol.	500	—
	Tri-EG	0·45	493	—
	Tetra-EG	0·80	425	—
	Hexa-EG	0·30	400	560

investigation to the corresponding values of polymers with a terephthaloyl-4-oxybenzoate (T-OB) mesogenic group with the same spacer. The ratios

$$R_M = \frac{T_M \text{ of polymer under investigation}}{T_M \text{ of corresponding T-OB polymer}}$$

and

$$R_C = \frac{T_M \text{ of polymer under investigation}}{T_C \text{ of corresponding T-OB polymer}}$$

were calculated when possible. The values of these ratios are given in table 3.

Some observations and conclusions may be made from the analysis of these data. The main observation is that both the R_M and R_C values are very close for polymers with different spacers for every polymer series. On the one hand this fact confirms that the synthesis of these polymers was carried out correctly. On the other it gives grounds to consider the average R_M and R_C values as the characteristic values which denote the mesogenic capability of every mesogenic group.

Table 3. R_M and R_C values for the polymers II–VI.

Mesogen		Spacer					
		$(CH_2)_{10}$	DiEG	TriEG	TetraEG	HexaEG	Average
T-OBP	R_M	1·22	1·21	1·18	1·24	1·25	1·22
	R_C	—	—	—	—	1·51	1·51
PT-OBP	R_M	0·86	0·98	0·85	0·86	0·83	0·87
	R_C	0·93	0·96	0·92	0·93	0·97	0·94
N-OB	R_M	1·00	1·02	1·04	1·02	1·05	1·03
	R_C	1·06	1·00	1·03	1·07	1·13	1·06
T-ON	R_M	0·98	0·96	0·97	0·93	0·94	0·95
	R_C	—	—	—	1·15	1·17	1·16
N-ON	R_M	1·08	1·05	1·05	1·02	1·03	1·05
	R_C	—	—	—	—	1·35	1·35

Table 4. Melting and clearing temperatures of LC polymers with five units in the mesogenic groups.

Mesogen	Spacer	T_M/K	T_C/K
-OBP-ON-T-ON-OBP-	PEG-1000	400	550
-OBP-ON-N-OB-OBP-	PEG-1000	440	545
-OBP-OB-T-OB-OBP-	PEG-1000	430	540
-OBP-OBP-T-OBP-OBP-	PEG-1000	480	above T_d
-OBP-OBP-PT-OBP-OBP-	PEG-1000	315	495

All the mesogenic groups may be arranged in order of their decreasing R_M and R_C values:

	T-OBP	N-ON	N-OB	T-OB	T-ON	PT-OBP
$R_M =$	1·22	1·05	1·03	1·00	0·95	0·87
	T-OBP	N-ON	T-ON	N-OB	T-OB	PT-OBP
$R_C =$	1·51	1·35	1·16	1·06	1·00	0·94

The question may be asked as to whether it is correct to compare the phase transition temperatures of polymers with a wide range of intrinsic viscosity values. We have shown that both the melting and clearing temperatures of $[TOB\text{-}0(CH_2)_{10}0]$ depend strongly on intrinsic viscosity values up to 0·30–0·40 dl g^{-1} which correspond to a M_W of approximately 8000 [5].

Similar regularities were observed for the other segmented aroyl-bis-oxyarylates. This fact allowed us to compare the phase transition temperatures with a sufficient degree of reliability.

The influence of molecular weight on the other thermodynamic parameters (ΔH_M and ΔH_C) is much more complicated and this is why these parameters are not discussed in the paper.

Analysis of phase transition temperatures of polymers with five single structural units in the mesogenic group confirms the general regularities discovered for triad-type polymers (see table 4).

Some definite semi-quantitative conclusions may be made about the role every single structural unit plays in the determination of polymer thermal properties. These data may be useful in the prediction of melting and clearing temperatures of newly designed LC polymers.

Of course we realize that the influence of each structural unit on polymer thermal properties may be different for polymers with different chain rigidity. In consequence such predictions may be correct only for polymers with mesogenic groups and spacers in a main chain.

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