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SYNTHONS AS BUILDING BLOCKS IN THE SYNTHESIS OF LIQUID CRYSTALLINE MULTIBLOCK COPOLYMERS

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Abstract: Synthetic approaches which allow to insert rather long fragments with exactly definite sequence of several single structural units into polymer chains are considered and summarized. The procedure consists in preliminary formation of such sequences in a form of bifunctional "complex monomer" (synthons) which may undergo a polycondensation with other single or complex monomer to form macromolecule with definite alternation of several single monomers. These synthetic approaches were used for the synthesis of LC multi-block copolymers with definite structure of rigid block.

INTRODUCTION

Many new types of unusual polymer structures were developed during two past decades. Syntheses of dendrimers, polymer tubes and other complex molecules attract interest of many chemists. Nevertheless, synthesis of linear macromolecules "with a predetermined sequence, like the synthesis of proteins and nucleic acids... is a major challenge to polymer science that will occupy many years" (Ref. 1).

Traditional methods of both chain- and step-growth polymerization processes give either random or alternative but not regular distribution of two monomers (repeating units) used in such polymerizations. The situation becomes more complicated and not predictable when three and more single structural units are used in formation of polymer chains.

The synthetic approach based on preliminary preparation of fragments of macromolecules (synthons) and their subsequent coupling is considered to be very fruitful. The main idea consists in formation of definite sequences of different single monomers in structure of synthons which should have functional groups capable to insert this sequence in polymer chain. The latter may be formed by homopolycondensation of a synthon or by its polycondensation with another single

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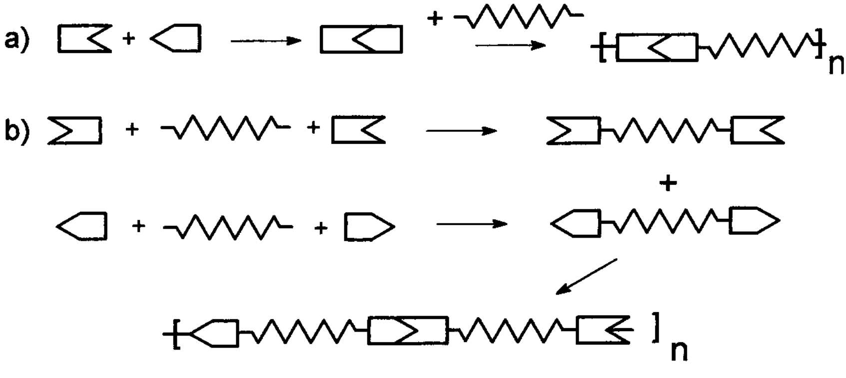
monomer or synthon. Both routes should give macromolecules with definite sequence of several single structural units along rather long fragments of its backbone. Similar approaches are used in synthesis of biopolymers — polypeptides and polynucleotides.

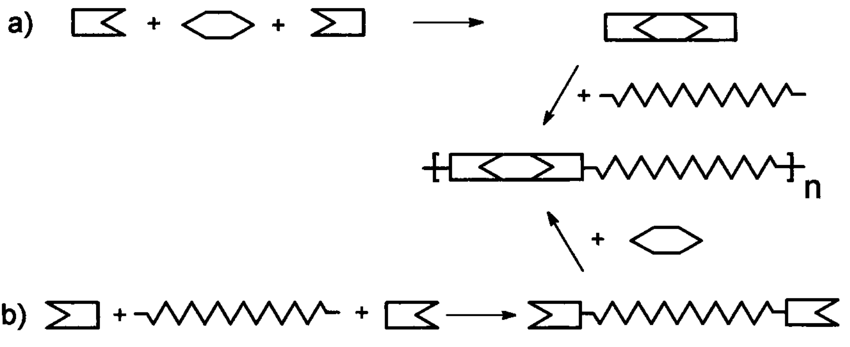
GENERAL CONSIDERATIONS

First the monomers containing the sequence *p*-(phenylene diamine) - terephthalic acid - *p*-(phenylene diamine) was used for synthesis of "ordered" polyamides whose properties were found to be different from those of random co-polymer by Preston in the late seventies (Ref. 2). At the same time syntheses of main-chain liquid crystalline (LC) polymers were started. They required insertion of rather complex chemical structures of low molecular weight (LMW) liquid crystals in polymer chains. Usually molecules of LMW LC consist of two (mesogenic diad) or three (mesogenic triad) *p*-phenylene (or 1,4-cyclohexylene) units joined by ester, amido, azo- or some other chemical bonds . In general case such conbination of single units is known as "mesogenic group". Thus, the task to prepare main-chain LC polymers came to formation of multiple repeated mesogenic groups along a polymer chains separated by flexible spacers. It could be solved by two-stage synthesis at least. First syntheses of synthons as monomers for main-chain LCP were reported by Roviello and Sirigu (Ref.3), Griffin (Ref. 4), Lenz (Ref. 5) and our team (Ref. 6).

Mesogenic groups of both diad and triad types may be formed either via synthesis of mesogenic monomer whose structure corresponds to that of mesogenic group (routes **a**, Schemes 1,2) or by formation of mesogen during polycondensation procedure (routes **b**, Schemes 1,2).



Scheme 1

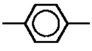
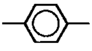
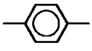
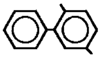
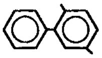
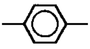
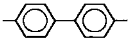
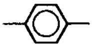
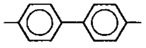


Scheme 2

Advantages and disadvantages of both routes were discussed in the literature (Ref. 7-8).

This work deals with generalization of approaches worked out by our team at the early stages of the investigation, with their further development and application for synthesis of LCP's with complex structure of their macromolecules such as amphpihilic LC multi-block copolymers. Our first synthons for synthesis of LC polymers were alkanoyl-dioxy-dibenzoyl dichlorides and terphthaloyl-dioxy-dibenzoyl dichloride (TOBC) **1a** (Ref. 9). The latter was found to be very promising in respect of synthesis of LCP due to its universality. A series of polymers may be prepared basing on the only monomer. The procedure of preparation of **1a** is very simple and ensures high yields of the product with excellent purity. LC polymers prepared by polycondensation of **1a** with aliphatic and aromatic diols were studied by different methods in detail. The convenience of **1a** for preparation of high-molecular weight LCP moved us to synthesize the series of synthons **1 b-f** with similar structure.

$$\mathbf{Cl\,CO — Ar^1 — OCO — Ar — COO — Ar^1 — COCl} \qquad \mathbf{(1)}$$

	1a	**1b**	**1c**	**1d**	**1e**	**1f**
Ar						
Ar¹						

A lot of LCP's were prepared with use of these synthons and aliphatic and oxyaliphatic diols in order to study the influence of fine chemical structure of the polymers on their phase transition temperatures and the contribution of each single unit in their thermal properties (Ref. 10).

Further development of this method has allowed to synthesize LC polymers containing more than three single monomers in mesogenic block. This problem was more difficult to solve. In general, combination of the routes of Schemes 1 and 2 makes possible to synthesize polymers with increased lengths of rigid blocks. Thus, combination of alkylene-aromatic synthons (routes b of Schemes 1 and 2) with synthons **1** gives LC polymers with increased length of rigid blocks which may be considered as LC multiblock copolymers. The most difficult step in their preparation was synthesis of the synthons containig rather long flexible block.

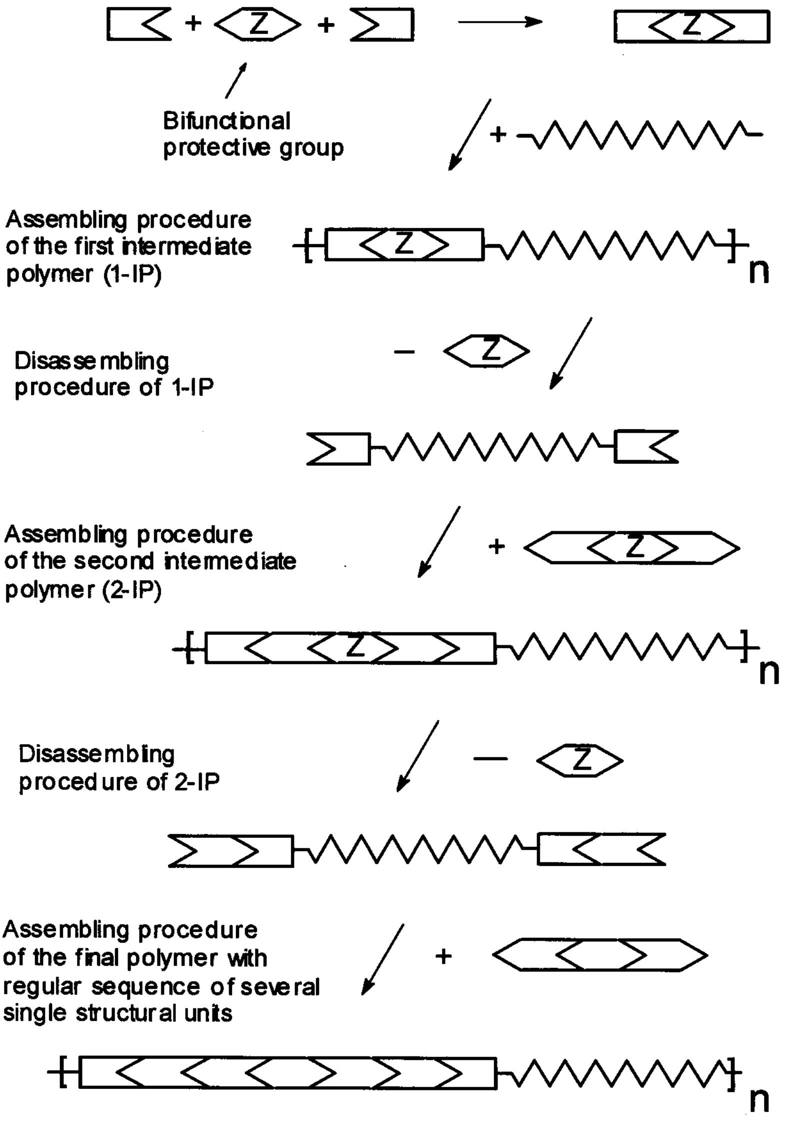
We have developed non-traditional approach to solve this problem (Ref. 11). In general view that is given at Scheme 3. The idea consists in a step-wise synthesis during which the intermediate polymer prepared from one synthon at the first step undergoes to selective degradation (disassembling) to form new synthon, different from the starting one. Single structural unit playing a role of bifunctional protective group is extracted from the chain during this degradation. Triad type synthon may be inserted in polymer chains instead of the extracted single unit at the second step (assembling of the intermediate polymer 2). The procedures of extraction of single units from the chains and their replacing by complex synthons may be repeated up to formation of any desired sequence of single units in repeating fragment of macromolecule.

This approach allowed us to develop the synthesis of LC multiblock copolymers which consist of flexible blocks with molecular weights above 1000 and rigid mesogenic blocks with definite length and sequence of single monomers.

SYNTHESIS AND PROPERTIES OF LC MULTIBLOCK COPOLYMERS

LC block and multiblock copolymers attract attention of many research teams due to their unusual properties, mainly due to their ability to undergo a microphase separation at relatively low molecular weights of the blocks (Ref. 12-14).

Poly(oxyethylene) (POE), poly(oxypropylene), polymethylene, and other flexible chains may play a role of flexible block. In our approach POE blocks are the most interesting ones because of their hydrophylity. Block copolymers combining hydrophylic POE blocks and hydrophobic rigid aromatic ones should be amphiphylic.


Z
Bifunctional protective group
Assembling procedure of the first intermediate polymer (1-IP)
n
Disassembling procedure of 1-IP
Assembling procedure of the second intermediate polymer (2-IP)
Disassembling procedure of 2-IP
Assembling procedure of the final polymer with regular sequence of several single structural units

Scheme 3

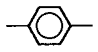
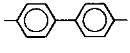
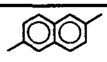
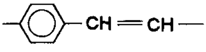
The most difficult part of these syntheses is preparation of synthons containing long flexible blocks. The matter is that hydroxyaroyl derivatives of POE have just the same solubility as polyethylene glycols and necessary intermediate compounds have. The problem was solved by realization of the idea considered in general form in Scheme 3. Bis-(hydroxyaroyl) derivatives of POE **(4)** necessary for synthesis of the multiblock coplymers were prepared via selective hydrolysis of intermediate polymer **(3)** whose structure includes the desired bis-oxyaroyl-(POE) sequences as repeating fragment. The intermediate polymer was prepared in its turn by polycondensation of special synthons **(2)** containing bifunctional protective group with poly(ethylene glycol)s.

The first publication in this area (Ref. 11) dealt with working out of the approach with use of *p*-phenylene rings as single structural units and oxalyl residue as central bifunctional protective group **(2a)**. Further development of the method was realized in synthesis of new synthons **(2b-d)** with central protective oxalyl group:

$$\underset{(2)}{\mathrm{Cl-CO-R-OCO-COO-R-COCl}} + \mathrm{HO-(POE\text{-}X)-OH} \longrightarrow$$

$$\longrightarrow \underset{(3)}{\mathrm{[-CO-R-OCO-COO-R-COO-(POE\text{-}X)-O-]}} \xrightarrow{\mathrm{OH}^-}$$

$$\longrightarrow \underset{(4)}{\mathrm{HO-R-COO-(POE\text{-}X)-OCO-R-OH}}$$

	2a	**2b**	**2c**	**2d**
R				

Polycondensation of **2 a-d** with polyethylene glycols with different molecular weights X gives intermediate polymers **3** whose selective hydrolysis results in formation of hydroxyaroyl derivatives of corresponding poly(oxyethylenes) **4**. They may serve as synthons for synthesis of intermediate polymer of the next generation **5** via polycondensation with synthons **2 a-d** or the final multiblock copolymers **7** via polycondensation with synthons **1 a-f**. Disassembling of **5** gives synthons **6** for synthesis of block copolymers **8** with seven single monomer units in rigid blocks and so on. Taking into account that each single monomer unit may contain more than one benzene ring, the total number of the latter may be high enough.

$$4 + 2^1 \rightarrow [\text{- CO - R - OCO - R}^1\text{ -OCO - COO - R}^1\text{ - COO - R-COO - (POE-X) - O -}]$$

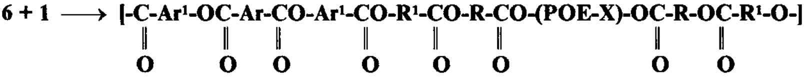
$$(5)$$

$$\downarrow$$

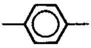
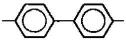
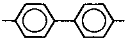
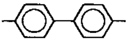
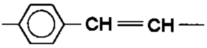
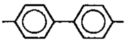
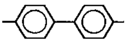
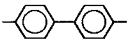
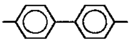
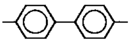
$$\text{HO — R}^1\text{ — COO — R — COO — (POE-X) — OCO — R — OCO — R}^1\text{ — OH}$$

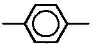
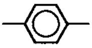
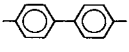
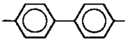
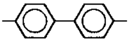
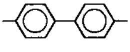
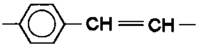
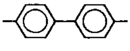
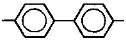
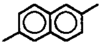
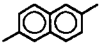
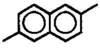
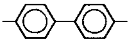
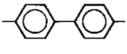
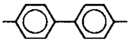
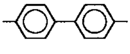
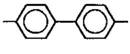
$$(6)$$

$$4 + 1 \longrightarrow [\text{-CO-Ar}^1\text{-OCO-Ar-COO-Ar}^1\text{-COO-R-COO-(POE-X)-OCO-R-O-}] \quad (7)$$



$$6+1 \longrightarrow [-\underset{\underset{O}{\|}}{C}-Ar^1-O\underset{\underset{O}{\|}}{C}-Ar-\underset{\underset{O}{\|}}{C}O-Ar^1-\underset{\underset{O}{\|}}{C}O-R^1-\underset{\underset{O}{\|}}{C}O-R-\underset{\underset{O}{\|}}{C}O-(POE\text{-}X)-O\underset{\underset{O}{\|}}{C}-R-O\underset{\underset{O}{\|}}{C}-R^1-O-] \quad (8)$$

	7 a	7 b	7 c	7 d	7 e
Ar					
Ar¹					
R					
X	1000	2000	4000	2000	2000

	8 a	8 b	8 c	8 d	8 e
Ar					
Ar¹					
R					
R¹					
X	2000	4000	2000	4000	4000

Several series of multiblock copolymers 7 and 8 containing POE-1000, 2000 and 4000 as flexible hydrophylic blocks were synthesized and some unusual features of their thermal behaviour were established. Content and sequence of single monomers for selected copolymers are given above.

The copolymers were studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction. Intrinsic viscosities values ($CHCl_3$, 25^0) and thermal properties of copolymers **7** and **8** are given in Table 1.

Table 1. Intrinsic viscosities values and thermal properties of copolymers **7** and **8**

Polymer	[η], dl/g	T_m,^{0}C DSC; 2-nd run	T_{fl}, ^{0}C POM/(DSC)	T_c, ^{0}C POM
7a	0.71	—	210/(208)	> T_d
7b	0.85	30	200/(183)	> 280
7c	0.38	44	130/	160
7d	0.48	31	122/(121)	170
7e	0.42	31	80/(87)	140
8a	0.46	40	240	> 300
8b	0.46	47	160	250
8c	0.32	29	165	245
8d	0.38	43	160	205
8e	0.32	43	75	120

Thermal properties of multiblock copolymers differ considerably from those of traditional type main-chain polymers. **7b** has the most symmetrical and anisometric rigid block in the series of copolymers **7 a-e**. That is why its thermograms display the most distinct peaks and may illustrate general regularities of thermal behaviour of the copolymers (Fig. 1). DSC curves of all copolymers with the exception of **7a** display distinct multiple (at the first heating run) or single (at the second run) endotherms at the temperatures below 50 ^{0}C (Fig. 1-2). These peaks correlate with disappearance of spherolytic patterns at polarizing microscopy pictures similar to that in melting of polyethylene glycols. This fact gives grounds to attribute these peaks to separate melting of POE blocks microphase. Changes in enthalpy for **7b** is 43 J/g. At the temperatures above this melting temperature the samples do not flow saving their shape when covering slide is shifted. They may be deformed under pressing onto the slide but this deformation is reversible. In general, the samples behave and look as anisotropic rubbers. Such state of the samples retains up to the small endotherm at DSC curves at flow temperature (T_{fl}) which is considerably higher than T_m. Above T_{fl} the cover slip may be easily shifted and the sample looks as typical anisotropic polymer melt. *ΔH* of this transition is 7.2 J/g for **7b.**

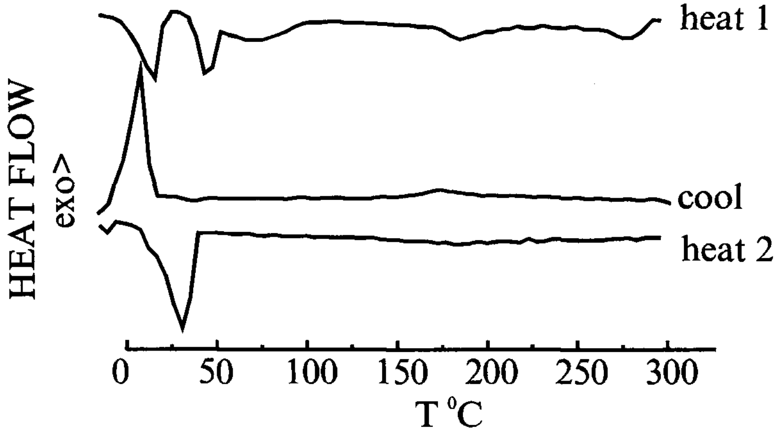


Fig. 1. DSC curves of copolymer **7b** , [η]=0.85 dl/g, scanning rate 8 °C/min

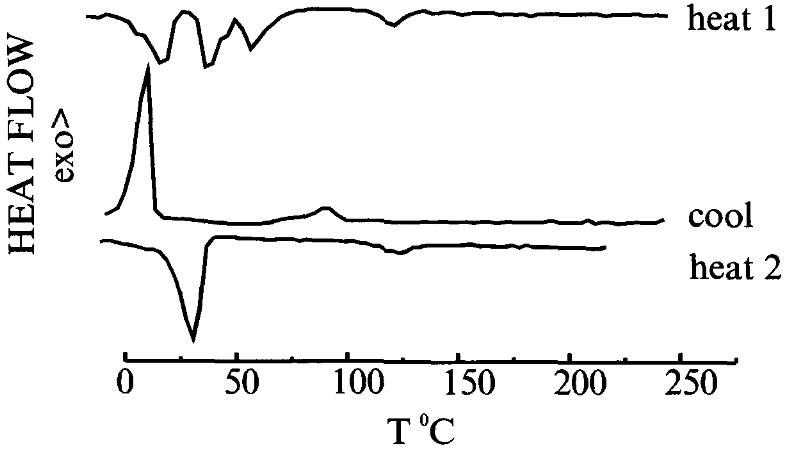


Fig. 2. DSC curves of copolymer **7d** [η]=0.48 dl/g, scanning rate 8 °C/min

It may be attributed to separate melting of aromatic anisotropic microphase. The sample becomes transparent and losses birefringence at clearing temperature (T_c) which is revealed at DSC curves for **7b** only (ΔH=3.2 J/g). In the second heating run the peaks corresponding to flow and clearing transitions become less distinct probably due to some degradation taking place in the first heating run.

Decrease in symmetry and anisometry of rigid block as a result of replacing of 1,4-biphenylene group to 2,6-naphthylene (copolymer **7d**, Fig. 2) leads to decrease in temperatures and changes in enthalpy of both flow and clearing transitions but not in POE microphase melting. The peak corresponding to clearing temperature is not displayed in the first heating run at all.

Increase in flexible block length from 2000 to 4000 (**7c, 8b,d-e**) results in increase of T_m by about 15^0 and decrease of both T_{fl} and T_c (Table 1).

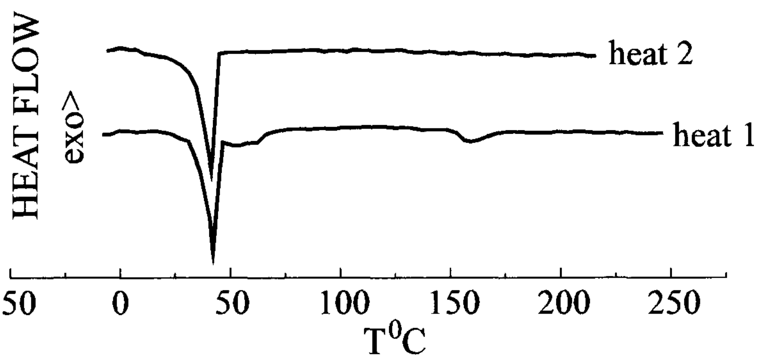


Fig. 3. DSC curves of copolymer **8d** [η]=0. 38 dl/g, scanning rate 8 ^{0}C/min

The most interesting feature in thermal behaviour of the copolymers is disappearing of birefringence during cooling runs. The melts under cooling from isotropic state in crossed polarizers first becomes bright, but after dropping temperature down birefringence disappeares and the melt becomes dark. The birefringence appears again at several degrees above crystallization of the POE microphase. This phenomenon is more characteristic for copolymers with POE-4000 flexible block and has not been explained yet.

X-ray diffractograms were made for samples of **7b** and **7c** at different temperatures. X-ray diffraction pattern of copolymer **7b** has one distinct reflection in small angles with d=80 A and two weak reflections in wide angles (Table 2). On heating after melting of POE-blocks additional multiple reflections appear in wide angles and retain up to clearing temperature. These reflections result from additional ordering of mesogenic blocks. The structure of polymer in solid state and mesophase is determined mainly by alignment of mesogenic blocks and flexible chains arranged between them.

Table 2. X-ray investigation of **7b** and **7c** at different temperatures:

Polymer	Temperature ^{0}C	Interplanar distances d(Å)							
7b	20 (as-prepared sample)	88.5			4.5		3.7		
	155		5.4		4.5	4.0	3.6	3.3	3.1
	200		5.4	5.0	4.5	4.0	3.6	3.3	3.1
	230		5.2	5.0	4.5	4.1	3.6	3.3	3.1
7c	20 (as-prepared sample)	6.3	5.7	4.9	4.5	3.7	3.3		
	60				4.4	3.8			
	140				4.4	3.8			
	20 (cooled)	6.3	5.7	4.9	4.5	3.7	3.3		

Copolymer **7c** with the same mesogenic block and POE-4000 flexible block forms weakly anisotropic melt. In contrast with polymer **7b**, the X-ray diffraction pattern of this polymer displays multiple reflections in wide angles at room temperature. Most of them disappear when the polymer sample is heated above the temperature of POE-blocks melting. With further heating the new reflections do not appear; that may be explained by not enough sufficient length of rigid blocks for formation of stable, highly ordered mesophase. Therefore the structural characteristics of polymer **7c** depend on the arrangement of flexible blocks. Rigid blocks are placed between long POE chains. Thus, the relationship between lengths of rigid and flexible blocks is a determining factor of polymer behaviour in melts.

Concluding discussion about properties of amphiphylic LC multiblock copolymers it is necessary to mention some specific features in behaviour of these polymers in respect to solvents. Their dual nature expands a number of solvents which they are solved in. The higher a ratio POE/rigid block, the wider a set of solvents for copolymers. Almost all polymers **7** are swellable in ethanol and methanol which usually do not interact with traditional type main-chain LC polymers. Besides, polymers **7** are soluble in THF, dioxane and their mixtures with water. All copolymers with POE-4000 flexible block except **8 b** are soluble in water.

The more detailed information about these interesting objects will be published later.

CONCLUSION

The considered approaches based on using of preliminary prepared synthons and assembling-disassembling procedure were demonstrated to be usefull in synthesis of polymers with complex structure. The capabilities of the approaches are not limited by use of hydroxyaromatic acids only. Other bifunctional single monomers may be inserted in polymer chain by this manner. Hybrid-type polymers consisting of single monomers of various chemical nature may be prepared by this way. The authors have started their experiments on insertion of natural α-aminoacids in the chains of LC polymers together with traditional hydroxyaromatic acids. The preliminary results will be published soon.

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