ISSN 1995-4212, Polymer Science, Series D, 2019, Vol. 12, No. 4, pp. 427–434. © Pleiades Publishing, Ltd., 2019.
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Thermotropic Liquid Crystalline Polyesters with Mesogenic Fragments Based on the *p*-Oxybenzoate Unit

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Received November 29, 2018; revised December 27, 2018; accepted January 17, 2019

Abstract—Main trends in the development of thermotropic liquid crystalline (LC) polymers based on *p*-hydroxybenzoic acid are described in this review. The relationship between the structure of the main chain of copolymers and their thermal and mechanical properties is shown. The possibility of creating biodegradable LC polymers is demonstrated.

Keywords: thermal resistant polymers, liquid crystalline polymers, polyesters, polycondensation

DOI: 10.1134/S1995421219040026

Liquid crystalline (LC) compounds are substances that combine an anisometric shape of molecules with rigidity of their structure. Due to such a structure, molecules acquire the ability to exhibit anisotropy of physical properties in the liquid state and form an ordered mesomorphic phase (mesophase or liquid crystalline phase). The rod-shaped molecules of calamitics, flat molecules of discotics, and recently discovered compounds with an exotic curved shape are examples of the molecular structure and shape of liquid crystalline compounds [1]. These compounds are capable of forming mesophases, which are classified, depending on the spatial arrangement of the molecules, into nematics, smectics, and cholesterics.

The first type of mesophases suggests the presence of a common direction of orientation of all molecules, the centers of gravity of which are located chaotically. In smectic LC compounds, the centers of gravity of molecules are arranged in layers, while the direction of molecular axes forms a certain angle with respect to an individual layer. The centers of gravity of cholesteric molecules are also arranged in separate layers, while the direction of molecular axes lies in the layer plane. With transition from one layer to the next one, the molecular axes turn to a certain angle and structures with helical ordering are formed in the bulk of the substance.

Depending on the factors affecting the emergence of mesophases, LC compounds are divided into thermotropic (that form mesophases in a certain temperature range) and lyotropic liquid crystals (that are formed upon dissolving in certain solvents).

Both low-molecular-weight compounds and macromolecules can undergo a phase transition into the LC state.

The beginning of the chemistry of LC polymers is considered to be the middle of the 20th century, when lyotropic aromatic polymers were first synthesized. Tens of thousands of liquid crystal polymers are known today. With scientific and technological progress, the interest of the scientific community in fundamental and applied developments in the field of LC macromolecules has been steadily increasing [2, 3]. This circumstance arises from the fact that new types of LC polymers with still unexplored properties are being created, that the specific properties of already-known polymers have been studied in detail, and that samples with properties that are very valuable for equipment and technology have been switched to an industrial level of production.

Depending on their structure, LC polymers may contain mesogenic groups in the main chain (as in the case of linear rigid chain polymers), in side chains (in comb-shaped polymers), and as part of a cross-linking agent (in polymer networks) [4]. Linear polymers with mesogenic groups in the main chain are characterized by high molecular rigidity and, as a result, are widely used as high-strength structural materials. The latter two types of LC polymers turned out to be promising materials in terms of their optical and film-forming properties.

Liquid crystalline polymers containing various functional groups attract fundamental interest. Such materials can exhibit electric conductivity or luminescent properties [5, 6], and contain ionogenic [7], photoactive, and electroactive groups [8, 9]. Thus, electroactive properties were found in polymers containing π-conjugates as mesogenic groups, and photoactive properties were observed in macromolecules containing azoaromatic fragments. Anisotropic polymers with ionic conductivity were obtained by incorporating the complexes of oligo(oxyethylene) links with inorganic salts into the spacer or the terminal group in lateral branches. Comb-shaped block copolymers have been studied as membranes in the processes of concentrating organic dyes from an aqueous medium [10].

In addition to mesogenic fragments covalently bonded in the main or side chains, noncovalent types of bonding of LC fragments in macromolecules have been developed in recent decades, the architectural design of which is based on the principles of supramolecular chemistry. This approach was implemented in polymers first synthesized by Kato, Frechet, and Len [7] by the formation of complementary hydrogen bonds.

In addition to linear chains, branched dendrimeric structures containing mesogenic groups can be formed [11, 12]. In this case, the occurrence of liquid-crystalline properties is determined by the presence of rigid-chain mesogenic fragments or segregation of macromolecules at the nanolevel. In the latter case, as a rule, the molecules do not contain mesogenic fragments in their composition. There are known options to include mesogenic fragments into the structure of spatially cross-linked polymers, which can later be used as structural materials.

Liquid crystalline properties of linear polymers were first observed in aromatic polyamides (aramids). Polymers of this class are referred to as "lyotropic polymers," i.e., ones that form a mesogenic phase when dissolved in highly polar solvents (for example, in sulfuric acid). High-modulus fibers made from aramid solutions contain oriented macromolecules, which explains their high strength characteristics.

The first samples of thermotropic LC polymers based on a homopolymer of *p*-hydroxybenzoic acid (4-HBA) were synthesized in the 1960s by Carborundum Co. [2]. It is noteworthy that this polymer required rather laborious processing conditions, namely, processing by sintering at a temperature of more than 400°C (the polymer did not exhibit thermoplastic properties). The technological difficulties that arose before engineers led to the search for new LC polymers that can be processed using methods that are standard for thermoplastic materials.

Subsequently, Du Pont developed a polymer derived from 4-HBA, 4,4'-dihydroxydiphenyl, and terephthalic acid, which is known under the brand name Ekkcel 1-2000 [13]. This copolyester is characterized by a relatively high processing temperature (injection molding method) of about 400°C. A number of LC polymers with lower processing temperatures, which are derived from the structure of this polymer and known under the trademark Xydar, were commercially released in 1985 by Amoco Chemical Co.

A lower temperature was required to process copolymers based on 4-HBA and polyethylene terephthalate, which are synthesized by Tennessee Eastman (brands X7G or Rodrun). Depending on the copolymer composition, the melting point varied from 230 to 300°C. The company Celanese obtained copolymers based on 4-HBA and 6-hydroxy-2-naphthoic acid, which are commercially available under the trademark Vectra, which combined processability and high thermophysical and strength characteristics.

The most common and thoroughly studied class of thermotropic LC polymers is aromatic polyesters based on aromatic diols, aromatic dicarboxylic acids, and aromatic hydroxy acids used as fragments of the polymer chain, which impart molecular rigidity to the molecule (Fig. 1). As a rule, such polyesters and copolyesters are obtained by polycondensation methods in the presence of acidic or basic catalysts (*p*-toluenesulfonic acid), metal oxides (antimony oxide), Lewis acids (titanium compounds, tin acetate), alcoholates, etc. [14].

The widespread industrial use of LC polyesters is attributable to their unique structural performance, i.e., a set of strength properties, impact resistance, chemical and radiation resistance, heat and temperature resistance, processability, etc. Of all types of polymers, only thermotropic aromatic polyesters have a complete set of the above characteristics. Polyesters containing mesogenic fragments in the main chain are considered to be a class of polymers that are resistant to extremely high temperature and mechanical loads [15–17]. The mechanical, thermal, and technological properties of LC polyesters substantially depend on the chemical nature of the main chain and macromolecular architecture [4, 5, 18–20].

When choosing a chemical structure for the macromolecular design of LC polyesters, one should take into account the individual characteristics of the physicochemical properties of individual classes of polymers the links of which will be included in their composition [2, 3, 13, 16, 21–23]. For manufacturing products from thermal resistant LC polymers, it is necessary for the samples to have a rather high melting point that should be below the oxidative decomposition temperature at the same time. Thus, LC polyesters containing sulfonic groups in the main chain have a set of valuable properties, as well as an unusually high strength and heat resistance [24–26].

It is known that oligomers have a slightly lower melting point than do polymer compounds. Depending on the presence of reactive functional groups at the chain ends, the subsequent formation of products from thermally resistant oligomers and their thermal processing contribute to an increase in the molecular

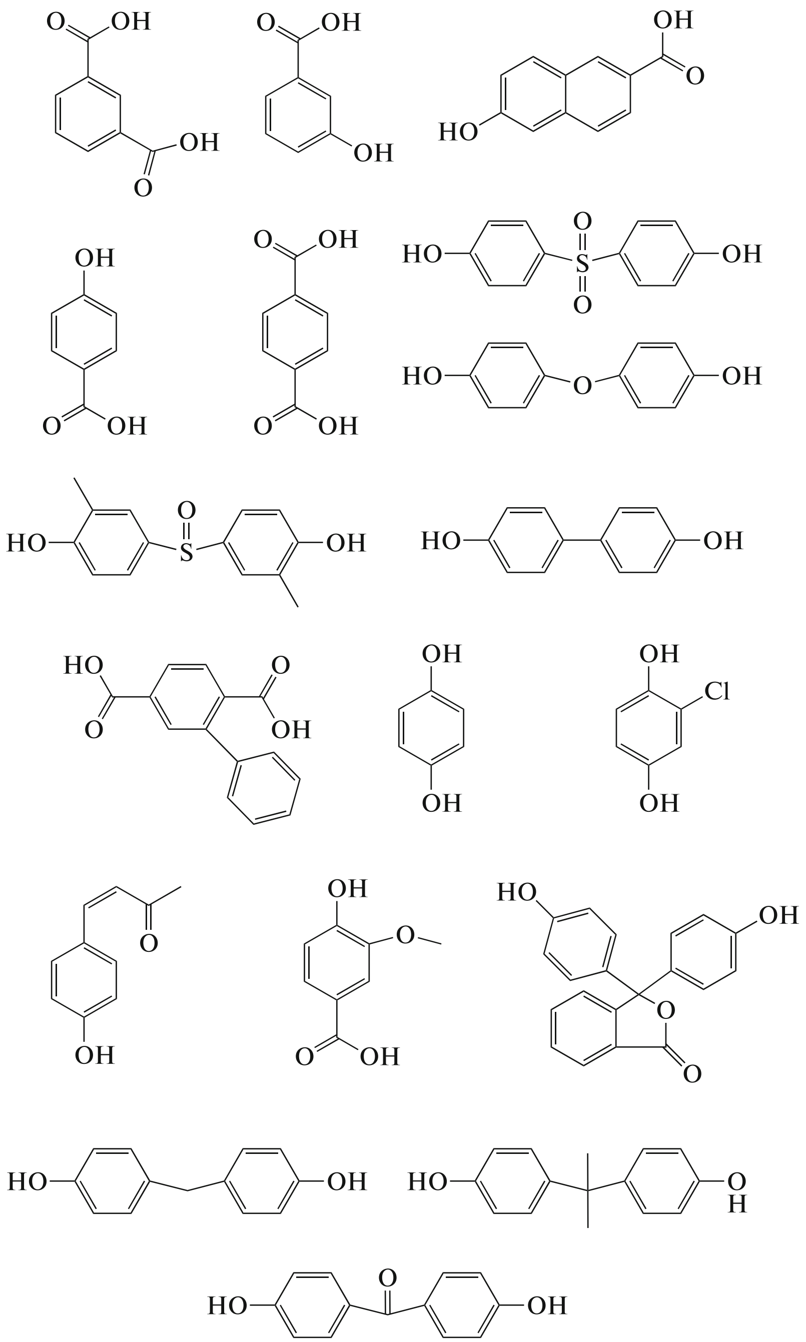

Fig. 1. Monomers used in the preparation of LC polyesters.

weight and the formation of a polymer with high thermal stability.

To form LC thermoplastic materials, polyesters must combine rigid aromatic fragments (mesogenic fragments) of the main chain with flexible fragments (spacers) in their structure. This requirement is due to the fact that completely aromatic rigid molecules (for example, poly-*p*-phenylene) have a melting point higher than their decomposition temperature. Consequently, their transition to a fluid state occurs at extremely high temperatures and accompanies by the decomposition of the material. A lower processing temperature is achieved by introducing flexible fragments into the main chain, which increase chain mobility, or by reducing intermolecular interactions between individual chains. The introduction of monomer links with different distances between ester groups into the macromolecule reduces the probability of intermolecular interaction between polar groups [16].

Another approach is based on the diverting macromolecules from a linear shape and the creation of bends or kinks in the main chain. The latter are formed by using monomers that have functional groups in the ortho- or meta-positions relative to each other. Thus, monomers based on derivatives of 2,6-naphthalene carboxylic acids are used in commercially available LC polyesters [27]. The presence of bulky substituents in the aromatic fragments of the chain also gives rise to a decrease in the interaction between macromolecules. The flexibility of substituents mainly affects the thermal stability and glass transition temperature. So, flexible chain substituents perform the function of a plasticizer, whereas rigid chain substituents lead to an increase in the glass transition temperature of the polymer.

Aromatic polyesters containing *p*-hydroxybenzoyl links are the most common type of thermotropic LC polyesters. Terephthalic acid, hydroquinone, and 4-HBA polyesters do not dissolve in organic solvents and have a melting point higher than their decomposition temperature [2, 3, 13, 16]. Some decrease in the melting point of the material is achieved by using monomer units with different distances between ester groups, as in the case of copolyesters, in which hydroquinone is partially replaced by 4,4'-dihydroxydiphenyl.

A new family of thermosetting oligomers based on 4-HBA was synthesized and investigated in [28]. The polymer chain contained para- and meta-substituted aromatic monomers, such as terephthalic acid, isophthalic acid, hydroquinone, resorcinol, bisphenol A, and 3-hydroxybenzoic acid. The synthesized oligomers with a molecular weight of 5000–9000 g/mol contained reactive functional groups and were obtained by melt polycondensation. Oligomers were cured by lengthening the chain and crosslinking in the temperature range of 310–400°C. As a result, nematic thermosetting polymers with a glass transition temperature of about 400°C were obtained. The polymers were characterized by high strength characteristics. This method made it possible to obtain materials that combine the easy moldability, high glass transition temperature, and excellent mechanical properties.

In [19], a series of aromatic polyesterimides based on N-(3'-hydroxyphenyl)-trimelithimide and 4-HBA was developed in order to create flexible films with a high glass transition temperature. Melt-extruded films made of either a high-molecular-weight polymer or oligomers were characterized by a glass transition temperature in the range from 200 to 242°C. After the orientation and stretching procedure at elevated temperatures, the films acquired extreme flexibility. Thermal treatment and orientation give rise to increases in both the glass transition temperature and the mechanical properties.

The temperature required for processing was achieved by introducing fragments into the macromolecule structure, which create a bend of a linear shape, often in combination with flexible spacers, such as the $-CR_2-$, $-O-$, $-S-$, and $-SO_2$ groups. Thus, thermotropic polyesters based on 4-HBA and 6-hydroxy-2-naphthoic acid were modified with terephthalic acid and bisphenol FE (2.5–10 mol %). The introduction of the latter into the main chain gave rise a decrease in the melting point from 260 to 220°C and an increase in the glass transition temperature from 70 to 118°C [29]. The oxidative degradation of the above polyesters modified with bisphenol A or bisphenol AF was studied using the thermogravimetric method, IR spectroscopy, and scanning electron microscopy. The energy of activation of thermal destruction of the sample containing bisphenol AF was higher than that of the original polyester. The least thermally stable was polyester containing bisphenol A links [30].

The ability to dissolve in a wide range of organic solvents, which is important in the preparation of film products by the irrigation, immersion, and centrifugation methods, was found in LC polyesters synthesized on the basis of 1,1-bis-(4-hydroxyphenyl)-1-phenylethane or 3,3',5,5'-tetramethylbisphenol A and aromatic acid chlorides by the method of interfacial polycondensation [31]. The glass transition temperature of polymer samples varied in the range of 165–202°C. The thermal stability of polyesters with a lateral phenyl group reached 480°C.

To improve the processability properties of the polymer based on 4-HBA, aromatic fragments connected with the links of the main monomer by means of ether bonds were introduced into its composition [32]. A lower melting point and degree of crystallinity are associated with a higher content of the flexible-chain component.

The thermal and thermomechanical properties of segmented polyesters with diphenyl units in the main chain depended on the number of methylene fragments in the spacer [33]. Young's modulus naturally decreased with an increase in the length of the spacer from 107 ± 12 to 19 ± 1 MPa.

In [34], information on the effect of the specific viscosity (an indicator characterizing the molecular weight of the polymer) on wear resistance is provided for thermotropic aromatic polyesters based on the following monomers: 4-acetoxybenzoic acid, diacetochlorohydroquinone, isophthalic acid, 6-hydroxy-2-naphthoic acid, and phenylhydroquinone diacetate for one type of LC polymers, and terephthalic and 4-acetoxybenzoic acids for another. It was concluded that a 4.4-fold increase in the specific viscosity in the second polymer leads to an increase in the wear resistance by factors of 1.2 and 13 when tested using abrasive particles and a steel counterbody, respectively. It was noted that the reinforcement of liquid crystalline polymers with carbon fibers up to 20 wt % provides the most dramatic improvement in tribological characteristics.

Copolyesters that are based on polyethylene terephthalate and 4-acetoxybenzoic acid were heterophasic systems. This is due to the bifunctionality of one of the components capable of involving into a polycondensation reaction with the formation of high-melting crystallites in the copolyester liquid crystalline matrix. The effect of the phase state on the mechanical properties of copolyester extrudates was studied [35]. The tensile strength of the extrudates was determined at room temperature on a constant-speed tensile viscometer. The results of the studies showed that the presence of a high-melting crystalline phase in an LC melt impairs the molecular orientation of the polymer chains and leads to a decrease in the strength characteristics of extrudates.

Various methods for producing aromatic polyesters based on 4-HBA derivatives are given in review [36]. For example, the addition of liquid crystalline copolyesters based on 4,4'-dioxydiphenyl diacetate and 4-acetoxybenzoic, isophthalic, and terephthalic acids to the aliphatic–aromatic polyamide mixture increases the viscosity and also the elasticity of the melt. Methods for preparing composites based on 4-HBA and polyethylene terephthalate with other polymers (polyacrylonitrile, phenyl-1,4-bis-(1-oxazoline), etc.) are reviewed.

The use of polyethylene terephthalate in the synthesis of polyesters allows one to reduce the viscosity of the melts and the molding temperature and to obtain cheaper products. It was noted that the introduction of any aliphatic fragments into the main chain of rigid chain polyesters reduces their physicomechanical characteristics. An increase in the tensile strength and the impact resistance is achieved by modifying the copolyester based on 4-HBA and polyethylene terephthalate with phenyl-1,3,5-tris-(2-oxazoline).

The properties of polyester compositions based on 4-HBA are analyzed in [37] and the areas of their application are specified. A composition containing polyglutharimide and a liquid crystalline polyester (3 : 1, respectively) based on 4-HBA, 4-aminophenol, and 6-hydroxy-2-naphthoic acid, had the increased strength and thermal resistance and could be used as a thickening agent for the adhesive and as a sealing agent. This composition was obtained by extrusion at 300°C. The polyester was synthesized from a mixture of 4-HBA, 4,4'-dihydroxydiphenyl, terephthalic acid, isophthalic acid, and acetic anhydride. After that, it was mixed with a copolymer of ethylene, glycidyl methacrylate, and methyl methacrylate in a ratio of 9 : 1 and molded at 291°C. The viscosity of the polyester composition melt was 29 300 cP, and its pour point was 255°C.

Items made of a composition based on an LC polyester and fluorocarbon polymer have high strength and tribological properties and are intended mainly for use in electronics and electrical engineering. Glass and carbon fibers can be added to the composition as fillers. The preparation of compositions of LC polyesters containing 4-HBA fragments with other polymers and various fillers leads to an increase in the strength and heat resistance and to improvement of mechanical properties. Such compositions can be used in the manufacture of structural parts, electrical insulation, cable connectors, and other items.

Polyethersulfones based on diphenylolpropane and phenolphthalein oligosulfones and terephthaloyl-di(*p*-hydroxybenzoic) acid dichloride have been synthesized [38] by means of acceptor–catalytic polycondensation. The thermogravimetric analysis data showed that the value of the 10% mass loss of the copolyester samples varies in the temperature range of 450–500°C. A high content of carbonyl groups leads to increases in the glass transition temperature and pour point and, accordingly, to a higher heat resistance of the material.

The combination of polysulfone and polyetherketone links improves the fluidity of the compositions during the extrusion process. In this regard, polyether sulfone ketones based on oligosulfone ketones or an equimolar mixture of oligosulfones and oligoketones were synthesized, the acidic components of which are mixtures of phthalic acids. The synthesis was carried out by the method of high-temperature polycondensation in an aprotic polar solvent medium in an inert gas atmosphere. The resulting polymers are characterized by high values of the tensile strength and plasticity.

Oligoformals were synthesized by polycondensation of aromatic bisphenols with methylene chloride in an alkaline medium, the subsequent reaction of which with terephthaloyl-di(*p*-hydroxybenzoic) acid dichloride gives new thermal resistant copolymers. Copolyesters are resistant to diluted and concentrated solutions of mineral acids and dissolve in chlorinated organic solvents and concentrated sulfuric acid. Strong and flexible films can be made from these polymers.

In [39], copolyesters of different composition were synthesized, which are modifications of phenolphthalein-based polyesters that contain 1 to 20 mol % of comonomeric modifying 3,5-dibromo-*p*-hydroxybenzoic acid residues from the total amount of phenolphthalein. The presence of 3,5-dibromo-*p*-hydroxybenzoic acid units in the macrochain increases the strength characteristics of copolyesters. The maximum breaking stress values correspond to polyesters with a modifier concentration of 5 and 10 mol %. The thermogravimetric analysis results showed that the presence of this modifier contributes to an increase in the temperature of thermooxidative degradation. The maximum decomposition temperature corresponds to the 10 mol % content of the modifying additive. The oxygen index increases with an increase in the content of 3,5-dibromo-*p*-hydroxybenzoic acid chloride in the polymer chain. The synthesized polyesters were relatively stable in dilute solutions of acids and alkalis.

Table 1. Thermal and mechanical properties of liquid crystalline polyesters

Sample	Initial decomposition temperature, °C	Tensile strength, MPa	Reference
Copolymers based on 4-HBA, 4-hydroxy-3-methoxybenzoic acid, and 2-hydroxypropanoic acid	340—364	—	[15]
Copolymers based on 4-HBA and N-(3'-hydroxyphenyl)trimellithimide	454—461	47—169	[19]
Copolymers based on 6-hydroxy-2-naphthoic acid, biphenyl-4,4'-dicarboxylic acid, and resorcinol	449—467	91—330	[21]
Copolymers based on 4-HBA, hydroquinone, and isophthalic acid	427—438	—	[38]
Copolymers based on 4-HBA, resorcinol, and terephthalic acid	450	—	[38]
Copolymers based on 4-HBA, 4,4'-dihydroxybiphenyl, and terephthalic acid	485—487	—	[38]
Copolymers based on 3-hydroxybenzoic acid, hydroquinone, and terephthalic acid	439—442	—	[38]
Copolymers based on 4-HBA, 2-hydroxy-6-naphthoic acid, terephthalic acid, and bisphenol AF	276—453	—	[29]
Copolymers based on 4-HBA and 2-hydroxy-6-naphthoic acid	432—507	—	[29]
Copolymers based on 4-HBA, 2-hydroxy-6-naphthoic acid, terephthalic acid, and bisphenol A	314—359	—	[30]
Copolymers based on 1,1-bis-(4-hydroxyphenyl)-1-phenylethane and terephthalic and isophthalic acid chlorides	480—483	—	[31]
Copolymers based on 3,3',5,5'-tetramethylbisphenol A and terephthalic and isophthalic acid chlorides	440—449	—	[31]
Copolymers based on bisphenol A and terephthalic and isophthalic acid chlorides	486—491	—	[31]
Copolymers based on 4-acetoxybenzoic acid, 1,4-diacetoxybenzene, and 1,3-bis (4'-carboxyphenoxy)benzene	416—424	—	[32]
Copolymers based on 3,5-dibromo-4-hydroxybenzoic acid, isophthalic acid, terephthalic acid, and phenolphthalein	370—424	100—115	[39]
Copolymers based on 4-acetoxybenzoic acid, 2,5-furandicarboxylic acid, suberic acid, 4,4'-diacetoxybiphenyl, 1,4-diacetoxybenzene, and 4-acetoxy-2-methoxybenzoic acid	370—412	17—51	[40]

Switching to biodegradable polymers is a current trend in polymer chemistry. From this point of view, 2,5-furandicarboxylic, suberic, and vanillic acids originally obtained from renewable sources appear to be promising monomers for preparing LC polymers. A number of new copolyesters with relatively low melting points were synthesized in [40] from suberic acid, 1,4-diacetoxybenzene, 4-hydroxy-3-methoxybenzoic acid, 4,4'-diacetoxybiphenyl, *p*-acetoxybenzoic acid, and 2,5-furandicarboxylic acid. The introduction of aliphatic fragments and links with alkyl substituents into the main chain of the macromolecule gave rise to a decrease in the melting point of polymers. As shown in Table 1, the presence of aliphatic fragments in the main chain somewhat reduces the thermal stability of thermotropic copolyesters.

Thus, a detailed analysis of the published sources confirms that the chemistry and technology of the production of liquid crystalline polymers have been progressively developing over the past decades. The use of methods and approaches of organic and supramolecular chemistry enables a wide variation and simulation of the architecture of LC polymers. However, research and development work should be focused, at the same time, on solving key issues and creating relatively cheap new materials possessing the physical and chemical stability for their successful industrial application.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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Translated by O. Kadkin