

**SELF-ASSOCIATION,
COMPATIBILITY, AND
STRENGTHENING BEHAVIOR
OF LIQUID CRYSTALLINE
OLIGOMERS**

**ANU
MOILANEN**

Department of Chemistry

OULU 1998



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LIQUID CRYSTALLINE OLIGOMERS**

Academic Dissertation to be presented with the assent of the Faculty of Science, University of Oulu, for public discussion in Kajaaninsali (Auditorium L 6), on December 19th, 1998, at 12 noon.

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ABSTRACT

Synthetic routes were developed for the preparation of 2-alkoxy-4-hydroxybenzoic acids and 2-alkoxyhydroquinones, and a large-scale synthesis was developed for the preparation of 2-thioalkoxyhydroquinones. The 2-alkoxy-4-hydroxybenzoic acids, which contained alkyl side chains of different length, were used in the synthesis of new main chain liquid crystalline (LC) homo-, random, and block co-oligomers. In addition, oligomers of terephthaloyl chloride and 2-thioalkoxyhydroquinones and oligomers of terephthaloyl chloride and 2-alkoxyhydroquinones were produced.

All the oligomers were blended with aliphatic polyamide 11 (PA 11). The effect of alkyl side chain length on the compatibility behavior of the LC oligomers towards the aliphatic polymer was characterized by DSC and FTIR, and the effect of side chain length on the flexural properties of the blends was investigated with a three-point bending test.

The miscibility studies showed variable interfacial adhesion between the blended compounds. The strongest adhesion was achieved between PA 11 and the homo-oligomers of 2-alkoxy-4-hydroxybenzoic acids with short or medium long substituents (C_4 - C_{10}), but the interactions between PA 11 and the oligomer with long aliphatic side chain (C_{18}) were poor, as were those between PA 11 and the wholly aromatic oligomer of 4-hydroxybenzoic acid. The compatibility between PA 11 and the co-oligomers of 2-alkoxy-4-hydroxybenzoic acids was slightly lower than the compatibility of the corresponding homo-oligomers. DSC and FTIR analyses of the blends of oligomers of terephthaloyl chloride and 2-thioalkoxyhydroquinones and oligomers of terephthaloyl chloride and 2-alkoxyhydroquinones with PA 11 implied that the interactions between the blended compounds were poor.

FTIR spectra and viscosity measurements confirmed that all the oligomeric structures could self-associate, with effect on the final mechanical properties of the polyamide. The strength of PA 11 in a three-point bending test was increased by the addition of only 1% of LC oligomers to the matrix. The results also showed that the strengthening ability of the oligomers is directly proportional to the total amount of aliphatic carbons. The best strengthening results were obtained with unsubstituted oligomers, random co-oligomers of 2-alkoxy-4-hydroxybenzoic acids, and homo-oligomer of 2-butoxy-4-hydroxybenzoic acid.

DSC investigations of a ternary blend of the oligomer of 2-decanyloxy-4-hydroxybenzoic acid, PA 11, and wholly aromatic commercial LC polymer showed the promising compatibilizing effect of the oligomer.

Keywords: liquid crystalline polymers, polymer blends, miscibility.

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Oulu, November 1998

Anu Moilanen

Symbols and abbreviations

| | |
|-------------------|--|
| BQ | = 1,4-benzoquinone |
| BnCl | = benzyl chloride |
| CDCl ₃ | = deuterated chloroform |
| σ_b | = stress at break |
| σ_y | = yield stress |
| DMF | = N,N-dimethylformamide |
| DSC | = differential scanning calorimetry |
| EGMA | = ethylene-glycidyl methacrylate |
| f | = volume fraction |
| FTIR | = fourier transform infrared spectroscopy |
| ΔH | = heat of fusion |
| HBA | = 4-hydroxybenzoic acid |
| HIQ | = poly(<i>p</i> -oxybenzoate-co- <i>p</i> -phenyleneisophthalate) |
| HQ | = hydroquinone |
| HRMS | = high resolution mass spectrum |
| LCP | = liquid crystalline polymer |
| M_w | = weight average molecular weight |
| MAP | = maleic-anhydride-grafted PP |
| MS | = mass spectroscopy |
| η | = viscosity |
| NMP | = 1-methyl-2-pyrrolidinone |
| NMR | = nuclear magnetic resonance |
| Noryl | = polymer blend of PS and PPO |
| PA 11 | = polyamide 11 |
| PA 6 | = polyamide 6 |
| PA 66 | = polyamide-6,6 |
| PAr | = polyarylate |
| PBT | = poly(butylene terephthalate) |
| PC | = polycarbonate |
| PEA | = poly(ether amide) |
| PEI | = poly(ether imide) |
| PEO | = poly(ethylene oxide) |
| PES | = polyethersulfone |
| PET | = poly(ethylene terephthalate) |

| | |
|-------------------|---|
| PHB | = poly(hydroxy benzoate) |
| PMMA | = poly(methyl methacrylate) |
| POB | = poly(oxybenzoate) |
| PP | = polypropylene |
| PPO | = poly(phenylene oxide) |
| PPS | = poly(phenylene sulfide) |
| i-PrOH | = 2-propanol |
| PS | = polystyrene |
| PS- <i>co</i> -AN | = poly(styrene- <i>co</i> -acrylonitrile) |
| PVC | = poly(vinylchloride) |
| PVPh | = poly(4-vinyl phenol) |
| <i>R</i> | = gas constant |
| <i>r</i> | = room temperature |
| SG | = styrene-glycidyl methacrylate |
| SEM | = scanning electron microscope |
| SPS | = sulfonated polystyrene |
| T_c | = clearing temperature |
| T_g | = glass transition temperature |
| T_i | = isotropization temperature |
| T_m | = melting temperature |
| THF | = tetrahydrofuran |
| TLC | = thin layer chromatography |
| <i>V</i> | = molar volume |
| χ | = interaction parameter |
| ϕ | = volume fraction |

List of original papers

This thesis is based on the following papers which are referred to in the text by their Roman numerals:

- I Hormi OEO & Moilanen AM (1996) Process for the preparation of substituted quinones and hydroquinones. Pat.Appl. PCT/FI96/00047.
- II Hormi OEO & Moilanen AM (1998) Experimental studies of Lewis acid catalyzed additions of long chained alcohols to activated 1,4-benzoquinone. Tetrahedron 54:1943.
- III Moilanen AM, Hormi OEO & Taskinen KA (1998) Unexpected strengthening of polyamide 11 with liquid crystalline oligomers of 2-alkoxy-4-hydroxybenzoic acids. 1. Accepted for publication in Macromolecules.
- IV Moilanen AM & Hormi OEO (1998) Unexpected strengthening of polyamide 11 with liquid crystalline co-oligomers of 2-alkoxy-4-hydroxybenzoic acids and 4-hydroxybenzoic acid. 2. Submitted.
- V Moilanen AM, Hormi OEO, Skrifvars M, Hyvärinen S & Sundholm F (1998) Unexpected strengthening of polyamide 11 with liquid crystalline oligomers of 2-thioalkoxyhydroquinones/2-alkoxyhydroquinones and terephthaloyl chloride. Submitted.

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Abstract

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1. Introduction

Low molecular weight liquid crystalline materials have been known for about one hundred years, while thermotropic liquid crystalline main chain polymers have attained prominence only in the last thirty years. The first full description of a polymer exhibiting thermotropic behavior appeared in the mid-seventies when copolymers of poly(ethylene terephthalate) and p-hydroxybenzoic acid were synthesized. Aromatic polyesters that exhibit thermotropic liquid crystalline behavior have attracted particular interest because of their many unique properties. The driving force behind the development of liquid crystal polymers (LCPs) has been the desire to replace metal components with engineering polymers, most notably in the automotive and aerospace sectors.

There is also a great deal of interest in the blending of thermotropic LCPs with common thermoplastics. Ever since the early 1980s when the first studies on polymer blends containing a LCP were reported, the subject has claimed wide and enthusiastic attention. The main benefit of blending LCPs with the conventional engineering plastics is the potential for improving the processability and mechanical performance of the plastic. The main problem in blending LCPs is that, owing to their high aromatic content, they typically exhibit low adhesion towards aliphatic polymers (1-2).

The poor interfacial adhesion between blended compounds results in less improvement in the mechanical properties than predicted by theory. Compatibilization is then necessary to enhance the adhesion between the two phases and so to improve the final properties of the blends. A well-compatibilized blend usually results in lower interfacial tension and finer dispersed domains (3).

The following five chapters provide a short review of liquid crystalline polymers and their blends with conventional thermoplastics, and an overview of the several techniques used to characterize the interactions between blended compounds. The main compatibilization methods that are applied to improve the adhesion in LCP/thermoplastic blends are then described.

The new work described in chapters 7-10 involved the design and synthesis of monomers and their use in oligomerizations of new liquid crystalline oligomers. The synthesized oligomers contain various amounts of carbon atoms in the side chain. The oligomers were solution blended with aliphatic polyamide 11 and the relationship was studied between the length of the flexible alkyl side chains in the rigid backbone of the LC oligomer and their miscibility behavior. Finally, the effect of the new liquid

crystalline oligomers on the flexural properties of polyamide was determined for oligomer-polyamide blends.

2. Liquid crystalline polymers

A liquid crystal, or mesophase, is a state of matter between the liquid and crystal states. Liquid crystals are ordered like crystals but flow like liquids. The responsible anisotropic entities are known as mesogens. Liquid crystals are either thermotropic, which means that they are liquid crystalline in the temperature range between melt and solid states, or lyotropic, which means that they form liquid crystals in concentrated solutions. The temperature at which phase transition from liquid crystal to melt state occurs is called the isotropization (T_i) or clearing temperature (T_c).

Liquid crystals are classified according to the shape of the mesogens and the structure and appearance of the mesophases. Mesogens are either rod-like or disk-like and they are divided into three main classes: nematic, smectic, and cholesteric. The main classes are further divided into subgroups.

The mesogenic units in a liquid crystalline polymer may be in the main chain or the side chain of the polymer. Polymeric liquid crystals are also classified according to their chemical structure and the conditions under which the LC state is formed. Main-chain LCPs may be either fully aromatic or built up of rigid mesogens and flexible spacers. In side-chain LCPs, the rigid mesogenic units usually are present in pendant side chains (Fig. 1) (4-6).

The main-chain LCPs are generally synthesized by polycondensation methods. Nematic structures are easy to produce since only large mesogens are required. Short mesogens connected by short flexible spacers are also possible. Smectic structures are usually obtained if rigid rod-like mesogens are present in periodic sequences or if mesogens of equal length are connected by large flexible spacers.

Radical polymerization of vinyl monomers is the most frequently used method for the synthesis of side-chain LCPs. The polymerization of suitable monomers and the reactions between mesogenic oligomers and flexible chains have also been utilized in the synthesis of side-chain LCPs (7).

Common liquid crystalline polymers are elongated cylinder-like molecules. Their anisotropy can be determined by the aspect ratio $x = L/D$, where L is the length and D the diameter of the molecule. The larger the aspect ratio, the greater is the tendency of the molecule to maintain a preferred orientation at temperatures higher than the melting point and, therefore, the wider is the temperature range of stability of the mesophase. Molecular rigidity is another important feature of LCPs. The molecules should not have a bent conformation (8).

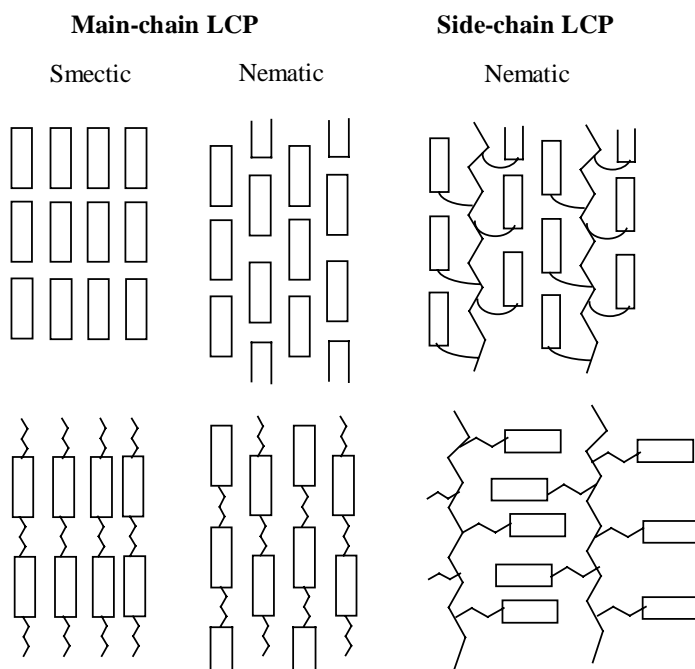


Fig. 1. Model structures of smectic and nematic rigid and semi-flexible main-chain LCPs and nematic side-chain LCPs where mesogens occur in pendant side chains.

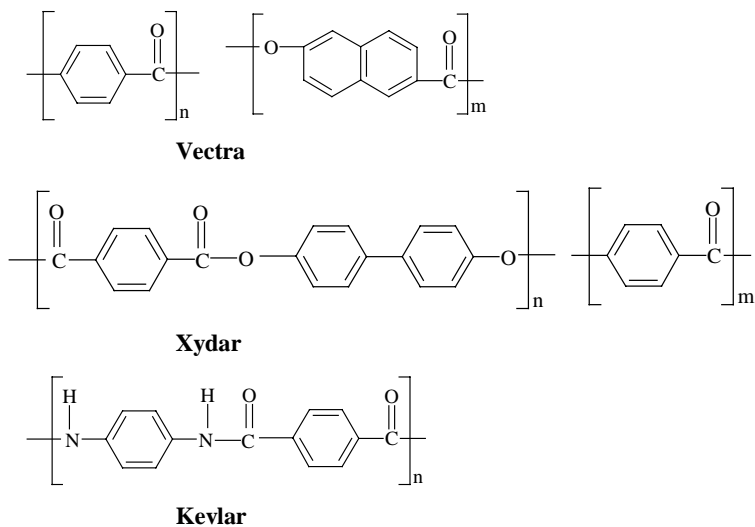


Fig. 2. Structures of commercially available LCPs: Vectra, Xydar, Kevlar.

Most commercial LCPs are copolyesters, copolyamides, or polyester-amides. LCP structures range from wholly aromatic to partially aliphatic and they have widely varying melting points. There are currently two major families of wholly aromatic thermotropic LCPs on the market: Vectra from Celanese and Xydar from Amoco Chemical Company (9,10). One of the most common commercially available lyotropic LCPs is Kevlar which contains terephthaloyl and para-phenylene diamide parts (Fig. 2) (11,12).

2.1. Temperature range and solubility problems of LCPs

The major drawbacks of rigid LCPs are their very high melting points and low solubility in common organic solvents (13).

In practice it is difficult to synthesize a wholly stiff macromolecule, because all macromolecules possess some degree of flexibility. Completely rigid rod-like molecules tend to be highly crystalline and intractable with melting points above the decomposition temperature of the polymers. The challenge with the thermotropic LCPs is to disrupt their regularity to the point at which mesomorphic behavior is achieved before the decomposition of the LCP. The requirements where the polymer must retain rod-like nature and at the same time be melt processable below decomposition temperature have by and large limited the thermotropic LCPs to polymers with linear ester or ester/amide bonds. In fact, most thermotropic LCPs are polyesters, because interactions between ester bonds are much weaker than the intermolecular hydrogen bonds of polyamides and the ester bond has less double bond character than does the amide bond. Both these features contribute to lower melting points of polyesters (7).

There are several ways to achieve the structural disorder effects in rigid-rod LCPs leading to lower glass transition, melting point and isotropization temperatures:

1. Create random distribution of unsymmetrical and symmetrical collinearly bonded structural units along the main chain.
2. Introduce crankshaft units to the polymer backbone or copolymerize with other mesogenic monomers.
3. Introduce mainly unsymmetrically substituted collinearly bonded structural units to the main chain.
4. Introduce "kinks" to the polymer backbone.
5. Add flexible spacer groups.
6. Incorporate aromatic ring structures of different length.

The modifications to the macromolecular backbone must be made without destroying the LC properties of the original material. A good example of such modification is the incorporation of substituted aromatic parts into the mesogenic units. The changes in the mesophase have the effect that the substituted compound can form only one mesophase with a low degree of molecular order, in contrast to the unsubstituted compound, which can have more than one.

Several groups of substituents (13-16) have been incorporated into the mesogenic phase of LCPs. Unfortunately, substituents which cause an increased polarizability and stronger dipolar interactions between the mesogenic groups often exhibit strong

intermolecular attractions, which could lead to higher melting points and clearing temperatures. Usually the transition temperatures of the substituted compounds have been lower than those of the unsubstituted parent compounds.

Kricheldorf *et al.* (17) synthesized new LC homo- and copolyesters (**1**, **2**) (Fig. 3) using substituted terephthalic acids and hydroquinone as the starting materials. The purpose of their work was to study the influence of the substituents on crystallinity, stability of mesophases, and solubility of the product polyesters in organic solvents. According to their results, almost all of the newly synthesized polymers formed a nematic phase above T_m . They also found the presence of halogenated phenoxy-terephthalic acids in the polymer backbone to have no significant effect on the segmental mobility of the homopolymers. The opposite result was obtained for copolyesters: copolyesters with halogenated phenoxy-terephthalic units showed significantly higher T_g s than the other copolyesters, evidently due to dipole-dipole interactions between halogens in the side chain and the ester group in the main chain. Clearly, the different steric situations in homo- and copolyesters is responsible for the difference. The good solubility of copolyesters **2b** and **2e** indicates that the inclusion of even one suitable substituent per repeating unit may have a dramatic effect on the solubility.

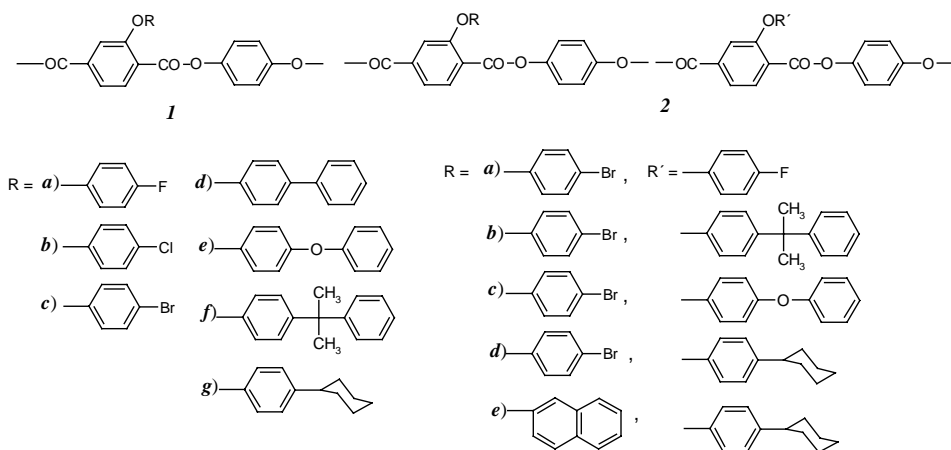


Fig. 3. The structures of LC homo- and copolyesters containing differently substituted terephthalate units (from Ref. 17).

In a comparison of the properties of aromatic polyesters (**3**) with different mesogenic units and a common flexible spacer (Fig. 4), Chen *et al.* (18) found that the structure of the para-substituted aromatic component based on an aromatic ester triad in the mesogenic unit has a dramatic effect on the liquid crystalline properties of the polymer. In the polymer containing a para-phenylene structure the decamethylene flexible spacer was able to remain essentially collinear with the mesogenic unit and could, therefore, be included in the nematic phase. The oxybiphenol structure in contrast, forced the spacer out of linearity disrupting the nematic phase in the process. LC mesophases were not formed in the polymer containing a meta-phenylene structure because of the nonlinearity of the structure.

Earlier studies (cited in Ref. 18) by the same group revealed that the length of the flexible spacers in polyesters of this type affects the liquid crystalline properties. They showed that if the spacer represents more than 40-50% of the weight of the repeating unit, the polymer cannot form a stable liquid crystalline phase.

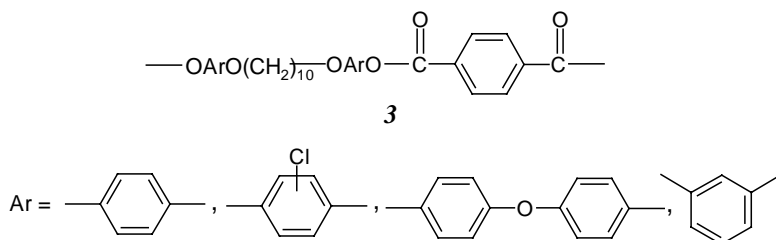


Fig. 4. Structures of aromatic polyesters with different mesogenic units and a common flexible spacer.

Zhou *et al.* (19) studied the thermal behavior of new LC polyesters containing alkyl substituents (**4**, Fig. 5) which they prepared from 1,10-bis(p-chloro-formylbenzolyloxy) decane and variously substituted hydroquinones. Their results showed both T_g and T_m to decrease with increasing amount of alkyl group in the side chain until a critical side chain length had been reached. The lowest transition temperatures (T_g, T_m, T_c) were usually observed in compounds with butyl or hexyl substituents. After the critical length ($n = 8$) had been achieved, T_m could also increase due to the crystallization of the side chains. The authors showed that even the addition of a methyl group to the polymer backbone caused a substantial decrease of T_i from 267 to 190 °C. Polymers that contained eight or more carbon atoms in substituents did not form stable liquid crystal phases.

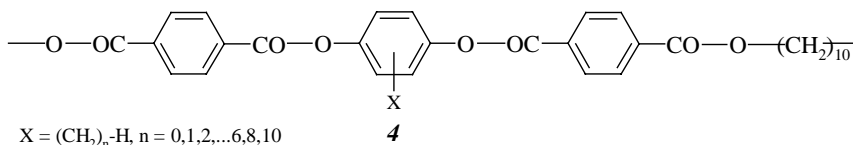


Fig. 5. Structures of LC polyesters containing alkyl substituents.

2.1.1. Hairy-rod polymers

Better solubilities in common organic solvents and structural disordering of LCPs may also be achieved by adding flexible aliphatic side chains to wholly rigid polymer backbone. These kinds of macromolecules are called hairy-rod polymers. The substituents, alkyl or alkoxy chains in the aromatic units of the backbone, reduce the melting temperature and improve the solubility of the polymers relative to the corresponding unsubstituted LCPs. In contrast to the ways to achieve structural disorder

effects discussed above, in hairy-rod polymers the rod-like structure of the main chain is fully preserved. The rigid-rod main chains are packed into a layered structure and the flexible side chains are arranged between the layers, forming paraffinic crystallites when the alkyl chains reach a critical length (Fig. 6). For example, poly(oxy-1,4-phenyleneoxy-2,5-dialkoxyterephthaloyl)s, where the length of the side chain is ≥ 8 , could form two-layered structure according to X-ray studies. Characterization of these polyesters indicated three phase transitions of first order: 1) transition of side-chains from crystalline to the solute phase, 2) formation of mesophase, and 3) transition of mesophase to the isotropic melt (20).

The combination of main chain rigidity and side chain flexibility results in a new class of materials with unique properties. Hairy-rod polymers are believed, for example, to be useful compounds for optoelectronics and membranes (21-24). Several studies on hairy-rod polymers are reported in the literature including ones on poly(3-n-alkyl-4-oxybenzoate)s (25), n-alkylated polyanilines (26), and poly(*p*-phenylene)s containing alkyl (27) and alkoxy substituents (28).

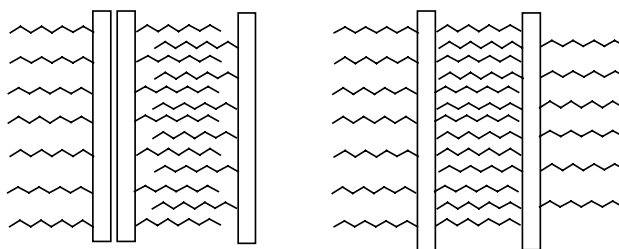


Fig. 6. Schematic illustration of hairy-rod polymers prepared from monosubstituted and disubstituted monomers.

2.2. Properties of thermotropic LCPs

Thermotropic LCPs, which are mainly random copolyesters and copolyesteramides, possess a unique combination of properties. The most significant characteristics are easy precision moldability, high outstanding dimensional stability and chemical resistance, low controllable coefficient of thermal expansion, low flammability and permeability, and exceptional strength, stiffness, and toughness (29).

In terms of commercial applications it is interesting to note that three classes of LCPs are emerging. The first is general-purpose LCPs that are exceptionally easy to process. These LCPs are possessed of high dimensional stability, molded-part repeatability, chemical resistance, good flame resistance, high strength, and good stiffness. The second class consists of LCPs that are more temperature-resistant and not quite as easy to process as the class I LCPs, but they have good dimensional stability, good chemical resistance, excellent flame resistance, and very good strength and stiffness properties. The third, lower-temperature/performance class consists of less expensive, less easily processed LCPs, which nevertheless have good dimensional stability, moderate chemical resistance, moderate flame resistance, good strength, and high stiffness (10).

2.3. Processing of LCPs

The good mechanical strength and dimensional and thermal stability of thermotropic LCPs are based on their fibrous structure. Mechanical properties, particularly tensile strength and stiffness, depend upon the degree of orientation and particle size achieved in processing. As the level of elongational flow increases the mechanical properties improve to very high tensile modulus and strength. A compression molded unoriented LCP has similar mechanical properties to conventional isotropic polymers (Fig. 7) (30,31).

All processes that utilize flow to orient polymer molecules have the following three requirements: 1) the material must be in liquid or liquid crystalline state, something that can be achieved either by heat or by adding a suitable solvent to the pure polymer, 2) the fluid must be forced to flow in a manner that causes the polymer chains to orient, 3) the fluid must solidify, either through cooling of the pure polymer or through removal of solvent from the polymer solution (4).

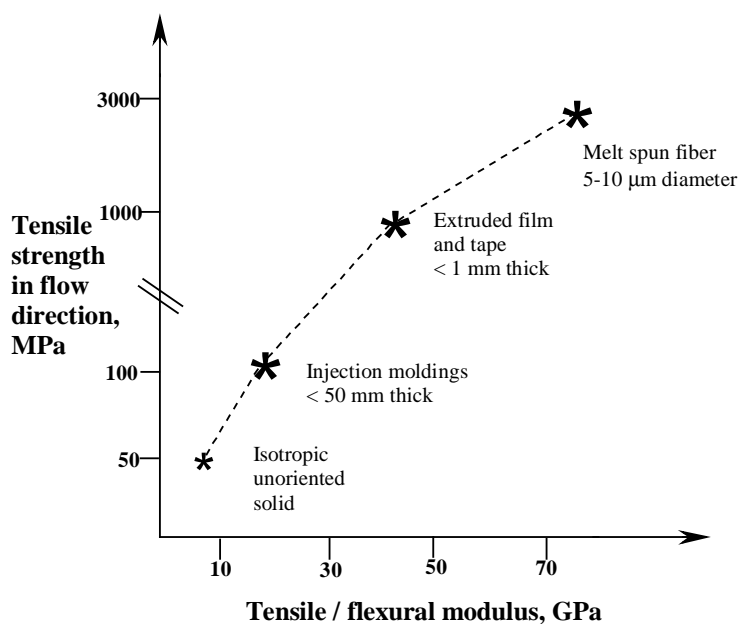


Fig. 7. Tensile strength vs. degree of orientation (from Ref. 30, copyright ©The Royal Society of Chemistry with permission).

2.4. Applications of LCPs

Their exceptional properties allow processed thermotropic LCPs to be used in a wide variety of applications: in sockets, chip barriers, bobbings, high temperature connectors, switches, vapor phase-components, and encapsulation of hybrid and microcircuitry in

the electronics/electrical industry; in pumps, tower packing, meters, down-hole oil well components, and valves in the chemical industry; in connectors, couplers, secondary reinforcing members, loose and tight buffers in fiber optic applications; in pulleys, bushings, bearings, seals, wear blocks, and mechanical components in industrial and mechanical applications; in fuel and electronic components and mechanical and under-hood components in the transportation industry, in interior components, fuel systems, radoms, brackets, fasteners, and electrical components in the aerospace industry; and also in housewares and sports equipment.

The excellent mechanical properties of LCP fibers have been exploited in protective fabrics (ballistic vests, gloves, clothing), strong fabrics (tarpaulins, conveyer belts), coated fabrics (inflatable boats, sails), industrial fibers (cables, ropes, filament wound pressure vessels), rubber reinforcement (radial tires, belts), plastic reinforcement (space applications, aircraft, boats, military helmets, sporting goods), cement reinforcement (building materials, pipes), friction materials and chemical alternatives to asbestos (brake linings, clutch facings, gaskets, packing) (10,29).

Despite the excellent properties and myriad applications of LCPs, one of the major brakes on LCP market expansion has been the relatively high cost of the polymers. Indeed, high cost has been the main incentive for seeking cheaper monomer syntheses and novel LC materials and blends.

3. LCP/thermoplastic blends

3.1. Advantages of blending

The development of totally new polymers is usually very expensive. There is an obvious pecuniary advantage, therefore, if the desired properties of materials can be realized simply by mixing two or more existing polymers. Adding LCPs to flexible thermoplastic polymers offers such an opportunity.

In general, the addition of only 10% of an LCP to a conventional thermoplastic approximately halves the melt viscosity of the polymer so that it becomes very much easier to process. Among the advantages of a lower processing temperature are reduced energy consumption and less degradation of polymers that are sensitive to high temperatures. Moreover, lowered viscosity facilitates the filling of large or complex molds (32).

Because LCPs have a more rigid molecular structure than conventional thermoplastics, and they generally exhibit a high degree of order in the melt under the conditions of shear and extension during processing, the LCP phase can deform into fibrillar domains, or fibrils, which can act as reinforcing elements in the blend. Reinforcement of thermoplastics through the addition of LCPs has been investigated thoroughly and many of the results are encouraging.

Self-reinforced thermoplastic blends based on thermotropic LCPs and commercial engineering thermoplastics have been studied intensively during recent years. The blends exhibit high strength and modulus, improved temperature and chemical resistance, low coefficient of thermal expansion, and improved barrier properties, and as such are suitable materials for products currently manufactured from pure LCPs. Blending is also considered as a possible route to overcome the highly anisotropic physical properties of LCPs (33-35).

Unfortunately, most of the available commercial thermoplastics are incompatible with the common, wholly aromatic LCPs, and the mechanical properties of blends in general have proved to be poorer than expected on the basis of the simple additivity rule (36,37).

3.2. Processing of blends

It has been shown that the improvement in the mechanical properties of thermoplastics when these are blended with LCP is associated with the fibrillar structure of the LCP. A number of processing and mixing techniques have been developed for the production of self-reinforcing LCP blends. These include fiber spinning, extrusion, film casting, thermoforming, and injection, compression, and blow molding. Injection molding and extrusion have been the two dominant processing operations in the search for suitable methods and conditions for optimal LCP fibrillations (38-40).

In a successful extrusion process the morphology of the LCP particles will range from spherical domains to thin fibrils (41). Spinning, where the LCP droplets are efficiently aligned with the elongational flow field, is an interesting method for processing high-performance thermoplastic/LCP blends. With their excellent mechanical properties, the LCP fibrils in the spun fibers are effective in improving the mechanical properties of the thermoplastic matrix in the drawing direction (42,43).

Easy molecular alignment is characteristic for liquid crystals and it often leads to highly anisotropic materials with poor transverse properties. Accordingly, thermoplastic blends typically show a marked increase in both tensile strength and modulus after processing, but simultaneously the elongation at break is drastically reduced. A further problem in blending LCPs and thermoplastics is that the majority of thermotropic LCPs have much higher melting points than thermoplastics. The blending is then difficult to carry out owing to the risk of degradation of the thermoplastic at high temperatures. New processing and mixing techniques such as multi-live feed molding and dual extruded mixing have recently been tested in an attempt to overcome these problems (33,34,44).

The mechanical properties achieved in the blends of thermotropic conventional polymers and LCPs are closely related to the fibrillar blend morphology, which in turn depends on processing method, and also on several other factors including miscibility between the LCP and thermoplastics, LCP concentration, blending temperature, blending time, viscosity ratio, and shear rate (43).

In most LCP/thermoplastic blends, shear rate has proved of particular importance. With increased shear rate, both tensile strength and modulus of the blend tend to increase. Likewise the processing temperature needs to be carefully selected. Blends prepared at temperatures near the LCP solid to mesophase transition generally exhibit better mechanical properties than those fabricated at significantly higher temperatures. The poorer properties at higher processing temperatures are due to the disintegration of LCP fibrils into droplets (44). Several research groups have investigated the effect of the viscosity ratio on the morphology. Most of the results indicate that the best fibrous structure is achieved when the viscosity ratio of the blend components is less than unity (44).

The degree of fiber formation depends on the concentration of LCP in the blend. Normally, a marked enhancement of mechanical properties is obtained only up to an addition of 20% LCP to the thermoplastic. Usually a small amount of LCP (0-15%) acts as a processing aid, and higher concentrations (15-85%) produce in situ composites and reinforced thermoplastics (36).

In studies of the effect of orientation on the final mechanical properties of PBT/LCP (60 HBA/40 PET) blends, Aji *et al.* (45) found that the addition of up to 30% LCP had no effect on the tensile modulus of unoriented samples, whereas a similar addition

improved the tensile modulus of oriented samples, in proportion to the amount of LCP in the matrix.

Several factors affecting the blend morphology have been investigated by Heino *et al.* (47). For example, in a study of the effect of viscosity ratio on LCP (Vectra A 950 and Rodrun LC-3000)/polypropylene (PP) blend morphology, they showed that the most fibrous structure was achieved when the ratio (LCP/PP) ranged from about 0.5 to 1. At higher viscosity ratios, LCP tended to appear in spherical or cluster-like domains, while at ratios lower than 0.5 the fiber structure was coarse.

Heino and coworkers (48) have also studied the effect of processing temperature on the final blend morphology, processing pre-blended PP/LCP (Vectra A 950 $T_m = 280\text{ }^\circ\text{C}$) at 180-200, 240 and 280 $^\circ\text{C}$ by extrusion or injection molding. A good reinforcing effect was achieved in the blends processed below 200 $^\circ\text{C}$ and in the melt blend. The blends processed at moderate temperatures showed cluster-like morphology and poor mechanical properties. Composite-like blend morphology was created at the processing temperature below T_m , and these blends exhibited impact strengths higher than those of melt processed blends. The melt processed blends possessed clearer skin/core morphology. On the other hand, at moderate processing temperatures, the LCP component was likely to deform and agglomerate to an undesirable morphology.

4. Interactions between blended polymers

The most common interactions between the components of physical polymer blends are secondary ones. These include dipole-dipole and van der Waals interactions and hydrogen bond formation, which normally are enhanced by effective mixing. In blends of polymers containing similar types of functional groups, molecular interchange reactions such as alcoholysis, acidolysis, and transesterification may be achieved in addition.

It is well known that compatibility between the phases of a blend will be increased if the two polymers are able to react with each other chemically. The most thoroughly investigated reaction is transesterification. The degree of transesterification is highly dependent on the reaction conditions, material preparation, temperature and duration of mixing, shear rate, and the presence of a suitable catalyst.

Typically, the components in chemical polymer blends are capable of both intramolecular interactions (self-association) and intermolecular interactions (inter-association). The adhesion between blended compounds will be poor if one of the components prefers self-association over inter-association (49). Etxeberria *et al.* (50) studied the two interactions in blends of poly(ethylene oxide) (PEO) with an aromatic poly(ether amide) (PEA), and found that the interactions between the carbonyl and NH groups of the polyamide and the intermolecular interactions between the NH groups of the polyamide and ether groups in PEO were proceeding simultaneously.

In an investigation of the effect of mixing time and catalyst addition on the compatibility of poly(ethyleneterephthalate) (PET)/LCP (Vectra A 950 and Rodrun LC-3000) blends, Heino *et al.* (51) showed that the polymers interact *via* transesterification, and that both factors affect the degree of interaction. They tested several catalysts and found by differential scanning calorimetry that the most desirable ones were zinc acetate and a mixture of zinc acetate and antimony trioxide.

In further studies on a three-component system of polyamide-6,6 (PA 66), PBT, and epoxy resin compatibilizer, Huang *et al.* (52) identified five possible reactions: i) condensation reaction between amine and carboxyl groups, ii) coupling reaction between amine and carboxyl with epoxide end groups, iii) coupling reaction between hydroxyl and epoxide end groups, iv) ester-amide interchange reaction, and v) alcohol interchange reaction between hydroxyl and ester groups (Fig. 8).

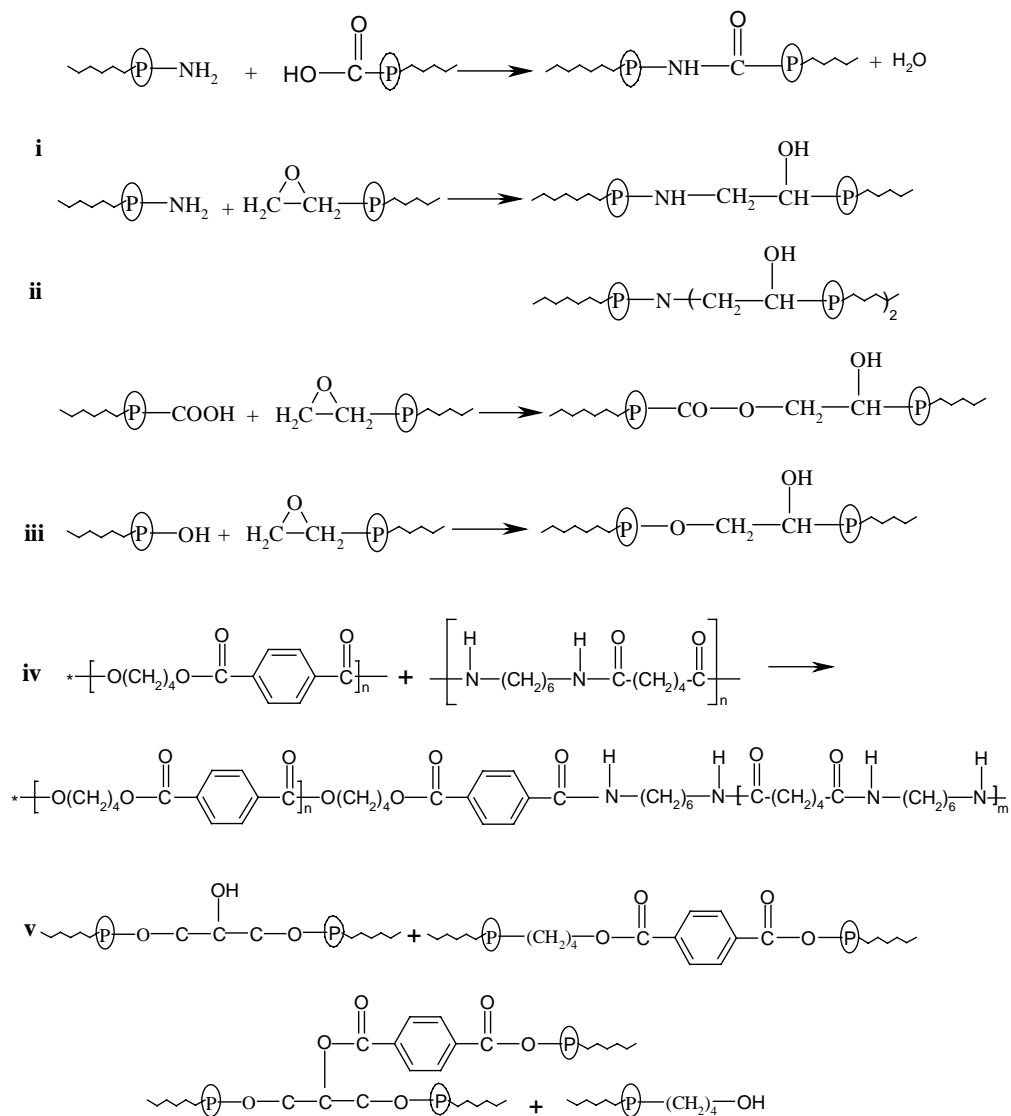


Fig. 8. Five possible reactions in a polyblend of PA 66, PBT, and epoxy resin compatibilizer.

5. Characterization of miscibility in polymer blends

The major problem in developing miscible polymer blends is to predict and characterize the miscibility. The most common instrumental techniques for characterizing polymer blends and their miscibility are differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), viscosity measurements, nuclear magnetic resonance spectroscopy (NMR), and various tests of mechanical properties. Basically the same methods can be applied for LCP/thermoplastic blends as for conventional blends.

Since characterization of the miscibility of polymers is seldom a straightforward matter, a good approach to identifying possible interactions between blended compounds is to compare the results obtained with the techniques noted above with the corresponding results for unoriented and uncompatibilized blends.

5.1. Differential scanning calorimetry

Differential scanning calorimetry is used to analyze the thermal transitions in polymer blends. Normally, miscible polymer blends are evidenced by a single T_g , or the T_g of one of the polymer components is shifted towards that of the other. In the case of LCP blends, however, the DSC traces of LCPs often fail to provide any useful information. Sometimes T_g s can not be observed at all, and if one or both polymers are crystalline, direct and reliable information will be hard to obtain.

Since both the degree of crystallinity and the melting point of a crystalline polymer can be expected to decrease with increasing content of the LCP component, indirect information on compatibility in LCP blends can be obtained from the melting and crystallization transitions. As has been noted in many miscible thermoplastic/LCP blends, a second component prevents the perfect crystallization of matrix and lowers its melting temperature (53-55). The addition of a small amount of LCP to a semi-crystalline thermoplastic actually enhances crystallization processes of the thermoplastic phase, apparently because LCP acts as a nucleating agent, causing the thermoplastic crystals to nucleate on the surface of the LCP domains (2,34).

In studies of the miscibility of blends of LC poly(*p*-oxybenzoate-co-*p*-phenyleneisophthalate) (HIQ) and polycarbonate (PC) by DSC, Wei *et al.* (56) found a

single glass transition temperature across the whole composition range. Subsequent annealing of the HIQ/PC blends at temperatures slightly above the melting point of HIQ revealed an immediate transesterification between the blend components. A T_g higher than the T_{gs} of the two pure components implied that HIQ had reacted with PC to give a new, amorphous polymer.

Using thermal tests, Kimura *et al.* (57) investigated in detail PBT/polyarylate (PAr) blends before and after transesterification. Solution blending was used to obtain samples without transesterification (physical blends), while heating of blends at 260 °C for 16 hours provided transesterified samples. A single T_g was found in the physical blends, lying between the T_{gs} of the pure components, and it increased with the PAr content; but there was no melting point depression for the matrix polymer, PBT. The miscibility of the compounds was explained by π -electron interactions between the terephthalate units, where the tetramethylene glycol parts in PBT provided flexibility to facilitate the interactions. In contrast, the transesterified blends exhibited a marked melting-point depression and a single but higher T_g than the corresponding physical blends. The authors explained that the blended polymers react to form block copolymer and then further to random copolymer, and this random copolymer has a higher T_g than the physical PBT/PAr blend.

The melting-point depression is an important property of crystalline polymer blends. In certain cases it is also possible to determine the polymer/polymer interaction parameter (χ) from melting point data, by using equation 1 below. The equation is suitable for blends where one of the components is crystalline.

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = - \frac{R V_2}{\Delta H_2 V_1} \chi (1-\phi_2)^2 \quad (1)$$

Here V_1 and V_2 are the molar volumes of the amorphous and crystalline polymer repeat units, R is the gas constant, ΔH_2 is the heat of fusion per mole of crystalline repeat units, T_m is the experimental melting point, T_m° is the maximum equilibrium melting temperature, ϕ is the volume fraction of crystallizable polymer, and χ is the polymer/polymer interaction parameter. The smaller the value of χ value the greater are the polymer/polymer interactions and the greater is the melting point depression (58,59).

It is important to note that this approach has been developed for equilibrium conditions. Two kinds of complications may arise if experimentally determined melting points are used. The first are associated with morphological variations in the composition, in which any variations in melting point due to morphology will be superimposed on the thermodynamic melting point depression. The second are related to processes such as lamellar reorganization, which may occur during the determination of melting points by techniques such as differential scanning calorimetry and differential thermal analysis (60).

5.2. Fourier transform infrared spectroscopy

The formation of compatible blends requires that the interactions between the unlike polymer chains be at least as favorable as the self-association of the component polymers. FTIR allows study of molecular interactions in a blend through comparison of the spectra of the blends and those of the component polymers. Normally the spectral differences will be evident as shifts in absorption frequencies, band broadening, and changes in band absorptivities. Among the techniques used to study miscibility, FTIR has the particular advantage of rapidity of analysis (61-64).

Etxeberria *et al.* (50) used FTIR to study the intra- and intermolecular interactions in PEA/PEO blends. The band in the range 1720-1620 cm^{-1} was assigned to the stretching vibration of the amide carbonyl group, with its broadness attributed to the partial superpositions of vibrations arising from two different states of the group. The signal at lower frequency was assigned to the free amide carbonyls and the other signal to the carbonyls involved in hydrogen bonding with NH groups (self-association). The spectra also showed a strong band in the 3320-3340 cm^{-1} region corresponding to the hydrogen-bonded NH and free NH groups at 3400-3450 cm^{-1} . As expected for miscible blends of PEA and PEO, the components interacted *via* hydrogen bonds, as could be inferred from the decrease in signal intensities of the H-bonded carbonyl involved in self-association and the free NH. The intensity of the latter signal decreased rapidly as the mixture became richer in PEO, and finally disappeared. Etxeberria and co-workers also analyzed the interactions between PEA and PEO through the stretching vibration of the C-O-C groups in the 1150-1085 cm^{-1} region.

Another example of FTIR analysis is the work of Pracella *et al.* (65). Using IR together with DSC, they showed that the polymer compatibility in poly(vinylchloride) (PVC)/ethylene-propylene copolymer blends can be enhanced through introduction of polar groups on to the macromolecular backbone. In investigations of the signals of carbonyl groups in blends of PVC and ethylene-propylene copolymers containing 4 and 10 wt % of ester groups in the side chain they found the shifts toward lower frequencies to be greater and the half widths larger in the PVC/10 wt % copolymer blends. This finding was attributed to the larger content of ester groups available for interactions with the methine hydrogens of PVC.

FTIR has also been utilized in quantitative analysis of chemical interactions between polymers. Li *et al.* (66) applied FTIR in quantitative analysis of hydrogen bonds between poly(methyl methacrylate) (PMMA) and poly(4-vinyl phenol) (PVPh), comparing the intensities of hydrogen bonded and free carbonyl signals of PMMA with the corresponding OH signals of PVPh in various PMMA/PVPh blends. In this way they were able to calculate the amount of hydrogen bonds between the components. They found, for instance, that less than 50% of the C=O groups of PMMA form hydrogen bonds with PVPh in the 1:1 blend.

FTIR has also been utilized for the mapping of different polymeric multiphase systems. Schäfer *et al.* (67), for example, prepared phase diagrams of PMMA/poly(styrene-*co*-acrylonitrile) (PS-*co*-AN) blends by determining the IR intensities of the carbonyl vibration of PMMA and the nitrile vibration of PS-*co*-AN and recording the chemical composition of the phases quantitatively as a function of annealing temperature.

5.3. Scanning electron microscopy

Scanning electron microscopy (SEM) is the most widely used technique in the study of blends (68). The shape, distribution, and size of the LCP particles in the matrix depend on several factors, such as LCP content, viscosity ratios of the blend components, rheological characteristics of the matrix, and the processing conditions. In addition, the morphology is affected by interfacial adhesion between the components. The interfaces are sharp in polymer blends with poor adhesion. High porosity of the material is also an indication of low interfacial adhesion (69). In certain cases scanning electron micrographs have also given clear evidence of good interfacial adhesion. In miscible blends all the LCP particles have some matrix over their surfaces and there are no open rings around the particles of LCP. Typically, the diameter of an LCP particle size in miscible blends is less than 1 μm , while the diameter in immiscible blends is 1 to 5 μm or larger (70).

Many researchers have attempted to link the mechanical properties of blends to the morphology of the LCP domains. Thus, a good reinforcement is achieved when LCP phases are well deformed and elongated during processing. The shape and orientation are retained during solidification and fibers are permanently oriented in the flow direction (71).

5.4. Viscosity measurements

Viscosity measurements have been utilized for estimation of the compatibility of thermoplastic and LCP in solution. In solution, repulsive interactions tend to cause shrinkage of the polymer coils, resulting in a lower viscosity value for the blend than the value calculated by the additivity rule from the viscosities of the pure blend components. Attractive interactions between the blended compounds increase the viscosity of the system (72).

La Mantia *et al.* (3) investigated the compatibilization of polyolefin and a semirigid liquid crystalline polymer, utilizing viscosity measurements to study the interactions between compatibilized and uncompatibilized blends of PE and LCP (SBH). Maleic anhydride based compounds were added as compatibilizers. All the compatibilized blends were found to generate flow curves slightly higher than those of uncompatibilized blends. The small increase in viscosity they ascribed to the presence of polar interactions, such as hydrogen bonding, between the components, which were taken to prove some compatibilizing action of the couplers. The experimental flow curves were also compared with those calculated from the additivity rule (eq. 2)

$$\eta_t = \eta_B f_B + \eta_C f_C \quad (2)$$

where η_t is the additive viscosity of the ternary blend, η_B is the viscosity of the binary blend, η_C is the viscosity of the compatibilizer and f is the volume fractions of the components in the blend. The authors showed that in the case of strongly incompatible

blends the experimental viscosity values were generally lower than those evaluated by the linear rule.

5.5. Nuclear magnetic resonance spectroscopy

The interactions between blended polymers have also been studied by nuclear magnetic resonance spectroscopy (NMR). Wei and coworkers (56), for example, have studied the transesterification reaction between liquid crystalline HIQ and PC by measuring the ^1H spectra of blends in a mixed solvent of deuterated trifluoroacetic acid and dichloromethane. Two-dimensional ^1H - ^1H COSY indicated that in samples annealed for 12 minutes at 310 °C the bisphenol-A in PC had reacted with the isophthalate and oxybenzoate in HIQ. Model compounds were used to identify the reactions.

Since the solubility of LCPs in organic solvents is normally poor the solid-state NMR methods have become an important tool in structural investigations of LCPs and their blends. Secondary interactions such as hydrogen bonding and charge-transfer interactions will tend to cause changes in ^{13}C chemical shifts, as the carbons involved in interaction experience changes in the surrounding electron density. At the same time the interactions between blended compounds affect the molecular mobility. In miscible blends the interactions change the relaxation behavior so that the relaxation times average to an intermediate value between the relaxation times of the pure components.

The dependence of spin-lattice relaxation times on the mobility and internuclear distances provides a means for quantitative determination of the composition of different phases. In an inhomogeneous material, the spin-lattice relaxation times in rotating and laboratory frames are highly sensitive to the size of the domains. Selective information on the specific behavior of each component in the blend can be obtained by taking advantage of cross-polarization phenomena between proton and carbon 13 nuclei (73-75).

5.6. Mechanical tests for miscibility

Mechanical properties of polymer material can be roughly divided into strength (tensile strength and modulus) and toughness (tensile elongation and impact energy). Modification of the material often results in the improvement of one property at the expense of the other: it is unusual for both strength and toughness to be improved simultaneously through any form of modification.

A number of studies have considered the effect of LCP concentration on the mechanical properties. Generally the tensile strength and modulus of a thermoplastic matrix are enhanced with increasing amount of LCP, while elongation and Charpy impact strength in the transverse direction are decreased significantly. Most blends have marked strength and stiffness in the fiber direction, but are brittle in the transversal direction. The anisotropic structure of the blend has a negative influence on the impact strength in the transverse direction, mainly due to poor adhesion between the blend components (36,76).

6. Compatibilization

Compatibility is frequently defined as miscibility on a molecular scale. Another definition is that the polymer mixture does not exhibit phase separation, since most compatibilized blends contain very finely dispersed phases. Yet a third definition is that polymers are compatible when together they possess a desirable set of properties.

Compatibilization may influence the final blend properties in complex ways. One effect of compatibilization is to reduce the interfacial tension between the blend components, causing an emulsifying effect and leading to an extremely fine dispersion of one phase in the other. Another major effect is the increased adhesion at phase boundaries, which gives improved stress transfer. And another is the stabilization of the dispersed phase against growth during annealing (77).

Compatibilization of polymer blends can be achieved in three ways: 1) by applying reactive blending technology, 2) by adding a separate compatibilizer, and 3) by modifying the chemical structure of one or both of the blended compounds.

6.1. Polymer blends without compatibilizers

In many studies on LCP/thermoplastic blend useful binary blends have been produced merely through the application of appropriate processing techniques. No external compatibilizer has been added to the blend (40).

Kiss (71) describes the behavior of binary blends made from commercially available conventional isotropic polymers and LCPs, some of which were extruded to strands or injection molded to tensile bars. The extruded and injection molded blends had higher tensile strength, tensile modulus, flex strength, and flex modulus than the starting isotropic materials. At the same time reduction in the elongation to break was observed.

Heino *et al.* (41), in turn, describe the processing of binary blends of LCP (Vectra A 950) and PET, PP, poly(phenylene sulfide) (PPS), and PBT by injection molding or extrusion. In general, the LCP acted as mechanical reinforcement for the thermoplastics and improved their tensile properties markedly. Because of the poor interfacial adhesion between the blend components, however, the blends often proved more brittle than the matrices.

6.2. Polymer blends with compatibilizers

Although the highly oriented fiber structure and good properties of LCP can be transferred to flexible thermoplastic through the use of various processing techniques, addition of a compatibilizer is often necessary to enhance the adhesion between the two phases and improve the final impact properties of the blends.

Current research on LCP/thermoplastic blends is, indeed, heavily directed toward the addition of a compatibilizer (or coupler) as a means of improving the interaction between blend components. Typically these compatibilizers are functional/reactive polymers or monomers (reactive blending), block or graft copolymers, or polymers with liquid crystalline properties. Most are low molecular weight compounds or oligomers possessing low melting temperature, but also some monomeric multi-functional compounds are highly effective couplers in polymer blends (76). In many cases the addition of compatibilizer has a marked effect on phase dispersion and may cause a substantial improvement in the tensile elongation behavior. It is suggested that the compatibilizer selected should also reflect the end-use requirements of the blend, as the improvements in compatibility through interchange reactions will not always be advantageous. For example, an increase in ester-exchange reactions could prevent the benefits of adding LCP to the matrix polymer and lead to a material with reduced mechanical properties and lower crystallinity (52). Three factors are believed to be responsible for the lower modulus obtained in some compatibilized blend systems: i) the rubbery nature of the compatibilizer, ii) the droplet LCP morphology, and iii) the reduced matrix polymer crystallinity (78).

The reactive compatibilizers are polyfunctional reactants capable of reacting with polymers to produce chain extension, branching, or even crosslinking. At first sight it would seem an ideal approach to combine two blend components through a suitable multi-functional coupling agent. *In situ* formed mixed copolymer, containing segments identical with the base polymers, would behave as a highly effective compatibilizer for the blend. Unfortunately, this coupling agent strategy can be applied to only a limited number of polymer pairs, as several criteria have to be met for the strategy to succeed. Both base polymers must possess functional groups that are capable of interacting chemically with the coupler. The relative reactivities need to be similar. Likewise the miscibility between the coupler and the base polymers is relevant; if the coupler is significantly more miscible with component A than component B then the whole project fails, as the coupler will be completely consumed by component A before it has reacted with the B component. In fact, the most desirable coupler is one that is immiscible with both base polymers. An immiscible coupler tends to associate to the interphase of the blend and can then react with both components simultaneously to form the desired mixed copolymer.

A reactive coupler normally contains functional monomer units and the *in situ* formed copolymer is a nonspecific graft-type compatibilizer. Excessive grafting will result in highly branched comb-like graft copolymer or even in a crosslinked network which is less effective in compatibilization. A slightly grafted copolymer with one or a few grafts per chain is a more efficient compatibilizer than an excessively grafted one. Therefore, proper control of the graft reaction by optimizing the content of the reactive groups, selecting a suitable catalyst, and choosing the proper blending sequence and processing conditions is essential to achieving the desired performance of the final blend (79-81).

Both block and graft copolymer compatibilizers contain segments identical with segments in the blend components, allowing them to migrate to the interphase and reduce the tension between matrix and dispersed phase (82). The addition of an effective phase compatibilizer to an incompatible thermoplastic blend ideally will result in reduced interfacial tension in the melt, finer phase domains, increased interfacial adhesion, and enhanced toughness. Unfortunately the desired improvement in toughness is not always achieved. The two most important factors for ideal fibril reinforcement of thermoplastic/LCP blends are the formation of long and fine LCP fibrils within the thermoplastic matrix and increase in the interfacial adhesion. Too often, enhanced interfacial adhesion is obtained at the expense of LCP fibril formation (83).

The addition of compatibilizer to thermoplastic/LCP blends often also result in a decrease the number of fibrils, or tends to convert the LCP fibrils into droplet domains. Use of compatibilizing agents that are themselves liquid crystalline is a promising new approach that may lead to LCP blends without any fibril fragmentation during the processing (84).

6.2.1. Reactive/in situ compatibilization

A typical reactive compatibilizer is a copolymer C-X, in which the C segments are identical or miscible with component A and X is able to react with component B to form a nonspecific C-X-B block or graft copolymer in the resulting binary A/B blend. In many of the reactive copolymers used to compatibilize LCP/thermoplastic blends, the reactive parts are epoxy groups or maleic anhydride units.

Chiou *et al.* (78) recently studied *in situ* compatibilized PP/LCP (Vectra A 900) blends, using ethylene-glycidyl methacrylate (EGMA) copolymer as the reactive compatibilizer. The polyethylene segments of EGMA are miscible with PP, while the epoxy functional groups can react with the carboxylic acid or hydroxyl end-groups of the LCP to form an EGMA-g-LCP copolymer. The *in situ* formed EGMA-g-LCP copolymer resides along the interface and reduces the interfacial tension between the base polymers. The authors' use of ethyl triphenylphosphonium bromide as a catalyst promoted the grafting reaction and improved further the blend compatibilization. LCP fibril formation in the compatibilized blend was unfortunately poor, because of low interfacial tension and finer dispersed phase domains, even though enhanced interfacial adhesion was obtained. Lower PP crystallinity in the compatibilized blends reduced the tensile strength and modulus, while improved adhesion resulted in improved impact strength and tensile elongation.

Chang *et al.* (79) incorporated styrene-glycidyl methacrylate (SG) copolymer *in situ*-type compatibilizer in Noryl/LCP(Vectra A 950) blends and showed SG to be effective in improving the processability, increasing the heat deflection temperature, and enhancing the mechanical properties of the blends. The LCP fibers in the Noryl matrix of the compatibilized blends were finer and longer than those in uncompatibilized blends. The fibers tended to form lamellate domains with a greater interface contact area than the domains in the uncompatibilized blends. The presence of ethyl triphenylphosphonium bromide catalyst in the polymer mixture improved further the interaction between polymers.

Most effective reactive compatibilizers are low molecular weight copolymers or oligomers. Chin *et al.* (76), however, used commercially available tetra-functional epoxy monomer (tetraglycidyl-4',4'-diaminodiphenylmethane) as a reactive compatibilizer in blends of PET and LCP (Vectra A 900). They showed that four epoxide groups in one molecule have greater opportunity to couple with PET and LCP simultaneously than does a di-functional epoxy compound in the copolymerate. Only small amounts of epoxy compatibilizer in the blend were needed to bring about dramatic improvement in the adhesion of the blended polymers. Mechanical properties of the blends were also improved. The presence of epoxy coupler enhanced the formation of the *in situ* formed LCP fibrils and they became finer and better dispersed. Strength and toughness were enhanced simultaneously. The findings of Chin and co-workers are exceptional; for the fibril formation in compatibilized thermoplastic/LCP blends is usually reduced or even totally suppressed.

6.2.2. Block and graft copolymers as compatibilizers

The most desirable coupler would appear to be a compound that is incompatible with both base polymers but nevertheless interacts with both. Perhaps the most promising compatibilizers today are block and graft copolymers that have chemical structure and/or solubility parameters similar to those of the blended polymers (85).

Magagnini *et al.* (86) synthesized and analyzed a PE-g-LCP copolymer and used it as a compatibilization agent in blends of PE and LCP (SBH). The compatibilizer was produced by reaction between PE functionalized with carboxylic groups and SBH monomers (sebacic acid, 4,4'-dihydroxybiphenyl and 4-hydroxybenzoic acid). Preliminary morphological investigations showed the compatibilizing effect of the copolymer to be significant, and clear enhancement was obtained in the interfacial adhesion between aliphatic and aromatic polymers.

In other work Magagnini *et al.* (82) synthesized a new graft copolymer consisting of polypropylene backbone and LCP (SBH) branches, PP-g-LCP, and used it as a compatibilizer in blends of PE and LCP (SBH). SEM micrographs of the uncompatibilized blends indicated a complete incompatibility of the two phases, while a significantly finer dispersion of the LCP droplets was formed in the PP-g-LCP compatibilized blends. However the micrographs gave no clear indication of improved adhesion.

6.2.3. LCPs as compatibilizers

Rupture of the fibrillar reinforcing LCP phase is a frequent occurrence during the blending. In an attempt to solve this problem, Miller and Qin *et al.* (84,87) tested a compatibilizer that itself possessed liquid crystalline properties. During processing, the LC compatibilizer has a lubricating effect, yet at the same time promotes the interphase adhesion and blend dispersion in the final fiber. PP/LCP(Rodrun LC-3000) blends were

compatibilized with use of the graft side-chain liquid crystalline functional copolymer compatibilizers shown in Fig. 9.

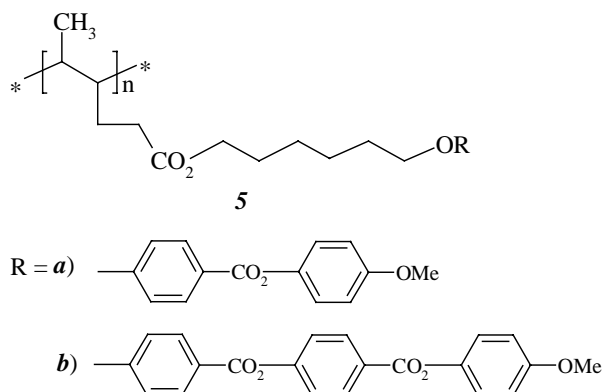


Fig. 9. Chemical structures of graft side-chain LCPs used as LC compatibilizers in PP/LCP blends (from Ref. 84).

LC compound **5b** was found to be an effective coupler, increasing the LCP fibril length, orientation, and dispersion. As well, a significant increase in the modulus and a small increase in tenacity were observed. The authors also found the effectiveness of the compatibilizer to be highly dependent upon the temperature range over which LC behavior is observed. Thus, the results were better with compatibilizer **5b**, which was in its LC phase during melt extrusion and hot drawing. Compatibilizer **5a**, whose liquid crystallinity occurs at a lower temperature than the processing temperature, had a detrimental effect on the final fiber properties.

Lee *et al.* (88) pursued the similar approach in using a second LCP as compatibilizer. Applying a two-step melt-blending process and PET/60% poly(hydroxybenzoate) (PHB60) as coupler, they prepared blends of wholly aromatic copolyester K161 and PC and PET. Morphological studies confirmed that the LCP could be finely dispersed and well bonded to an inherently incompatible PET matrix with use of a second LCP as compatibilizer. The adhesion obtained was probably associated with either partial miscibility of the blended compounds or chemical reaction of the intermediate layer with the thermoplastic matrix. The effectiveness of the coupling depended both on the absolute content of the compatibilizing phase and on the relative composition of the two LCPs. The uncompatibilized blends of K161 and PC were relatively unaffected by a cold-drawing process, while the cold-drawn compatibilized blends exhibited well-aligned LCP fibers.

Wei *et al.* (89) prepared a semi-rigid liquid crystalline copolymer, copoly(oxybenzoate-p-terephthalate)(60/40) (POB-PET) and used it as a compatibilizer in of PEI/Vectra A 950 blends. Blending with POB-PET increased the interfacial adhesion between the immiscible polymers relative to that of the uncompatibilized blend. The tensile modulus of the binary and ternary blends of Vectra and PEI was higher than that of the pure PEI. But the ultimate tensile strength of the blends was lower than that of

pure PEI. Wei and co-workers interpreted the decrease in tensile strength as a failure in the interface adhesion between compounds. Addition of only small amounts of LC coupler (less than 5 phr) to the binary blend of PEI and Vectra resulted in good final properties, but when the amount of coupler increased to 7 phr, the mechanical properties worsened. This was explained by a critical concentration effect of the POB-PET coupler, which means that at 7 phr concentration the free copolymer chains tended to aggregate rather than migrate to the interface.

6.3. Modifications of LCP structures

A third way to modify the compatibility of blends is to modify one or both of the blend components, for example by introducing of polar groups to the macromolecular backbone or, in the case of LCP, incorporating aliphatic flexible spacers into the chains. Enhanced miscibility between hairy-rod polymers and thermoplastics has been achieved by this last method (90,91). Modifications may achieve other benefits simultaneously, benefits such as structural disorder effects in the LCP, the formation of stable thermotropic mesophases, and preservation of the fibrillar morphology of the LCP.

Chang *et al.* (92) synthesized two new thermotropic LCPs with flexible spacers, one of them with a flexible hexamethylene spacer in the main chain (**6**) and the other with bis-hexamethylene branches in the terephthaloyl group (**7**) (Fig. 10).

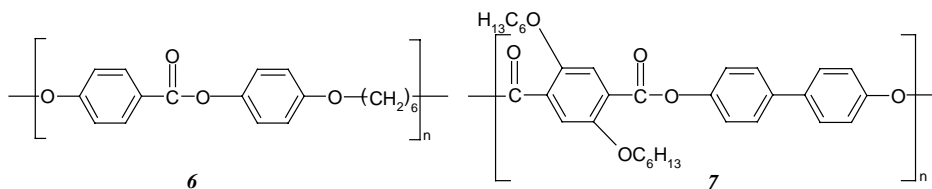


Fig. 10. Structures of thermotropic LCPs with flexible spacers in the main and side chains.

Different amounts of the LCPs were solution blended with poly(butylene terephthalate) (PBT) and the blends were melt-spun at different draw ratios. At all draw ratios the maximum enhancement in the ultimate tensile strength was observed for the blends containing only 5% LCP. At higher LCP concentrations, bigger spherical droplets were formed due to agglomeration of the LCP particles. The tensile properties were better for blends of polymer **7** than polymer **6** owing to the improved dispersion and finer fibrillar LCP.

Shin *et al.* (93) synthesized new thermotropic LCPs with long flexible spacers in the main chain and studied the effect of these on the mechanical and thermal properties and morphology of PET/LCP blends. They showed that the LCP domains deformed easily into a microfibrillar structure by shear flow, and also that the formation of microfibrils increased dramatically the initial modulus and the ultimate tensile strength of the blend.

Shin *et al.* (94) also synthesized the two new LCPs (**8**, **9**) with flexible spacers shown in Fig. 11.

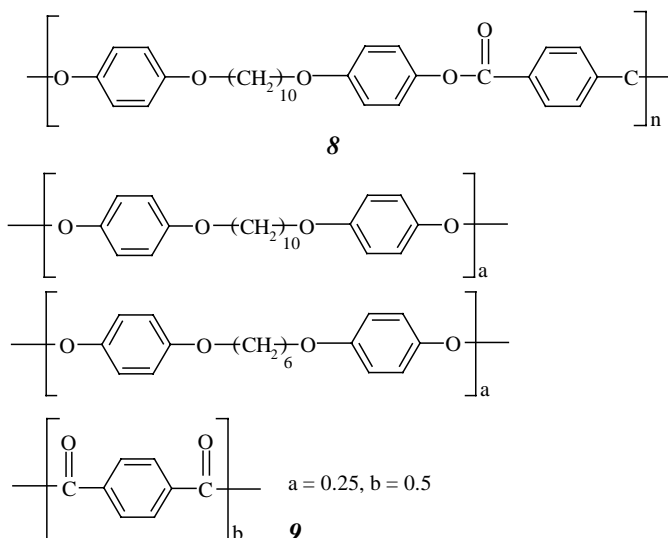


Fig. 11. Thermotropic LC homo- and copolymer with long flexible spacers in the main chain (from Ref. 94).

When these LCPs were blended with PET, the interfacial adhesion obtained was very good and the LCP domains deformed to microfibrils with large aspect ratios. For the drawn fibers the strength of the blend (30 wt % LCP) was about three- to four-fold that of pure PET. The PET/LC homopolymer **8** blend also showed more facile fiber formation than did the corresponding PET/LC copolymer **9** blend.

Although the modification of LCPs with flexible spacers is the most extensively used method to improve the interfacial adhesion between thermoplastics and LCPs, there are also other ways. Khan *et al.* (95), for example, synthesized LCP (**10**) containing $-\text{SO}_2-$ and $-\text{CO}_2-$ groups in each repeating unit in the hope that their new compound could improve the adhesion of LCP to PC, polystyrene (PS), and sulfonated polystyrene (SPS) *via* hydrogen bond formation between the polymer chains (Fig. 12).

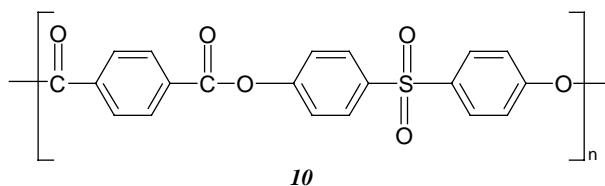


Fig. 12. LCP containing $-\text{SO}_2-$ and $-\text{CO}_2-$ groups in the repeating unit.

The results showed the LCP/PS and LCP/SPS blends to have a two-phase morphology with well-defined interfaces between the LCP and the thermoplastic. This indicates a poor interfacial adhesion between the blended compounds. The strengths of both blends decreased when the LCP content was increased. The strengths of LCP/SPS blends were slightly higher than those of LCP/PS blends, which indicates that sulfonation improves the adhesion between LCP and PS. Stronger adhesion between the LCP and PC resulted in a significant improvement in the mechanical behavior of PC upon LCP addition.

7. Aims of the study

As the previous chapters have shown, compatibilized blends of conventional thermoplastics and stiff liquid crystalline polymers have been an active area of research during recent years. In section 6.3 we saw that one approach to improving the adhesion between immiscible compounds involves modifying the structure of the LCP. The compatibility between aromatic LCPs and aliphatic thermoplastics can be improved through the incorporation of aliphatic flexible spacers into the LCP chains (90-94). Before the work described here, however, no systematic studies had been published on the effect of the alkyl side chain length on compatibility, and no investigations had been reported on the effect of the alkyl side chain length on the final flexural properties of blends.

There were three aims in my research: to study the effect of alkyl side chain length (C_0 - C_{18}) and the distribution of the alkyl side chains on the properties of LC oligomers; to study the effect of alkyl side chain length on the compatibility behavior of LC oligomers towards aliphatic polymer, and to study the effect of alkyl side chain length (C_0 - C_{18}) on the flexural properties of the LC oligomer/aliphatic polymer blends.

The work comprised the following steps:

1. To achieve the above objectives, synthetic routes were developed for the preparation of monomers containing various amounts of carbons in the side chains; specifically, routes were developed for the preparation of 2-alkoxy-4-hydroxybenzoic acids (2-alkoxyHBAs) (III) and 2-alkoxyhydroquinones (2-alkoxyHQs) (II). In addition, a larger-scale synthesis for the preparation of 2-thioalkoxyhydroquinones (2-thioalkoxyHQs) was carried out (I).
2. New main chain LC homo-oligomers and random and block co-oligomers of 2-alkoxyHBAs containing variable length alkyl side chains were synthesized (III-IV) and, in addition, oligomers of terephthaloyl chloride and 2-thioalkoxyHQs and oligomers of terephthaloyl chloride and 2-alkoxyHQs were produced (V).
3. All the synthesized oligomers were blended with aliphatic polyamide 11 (PA 11) and study was made of the effect of alkyl chain length and distribution in the oligomer backbone on the compatibility of the oligomer and aliphatic polymer.
4. A three-point bending test was used to evaluate the differences between blends prepared with various ratios of oligomer to PA 11. Study was made of the effect of alkyl chain length and distribution in the oligomer backbone on the final flexural properties of blends.

5. Finally, one of the oligomers was tested as a compatibilizer in an immiscible blend of LCP/PA 11.

8. Experimental

8.1. Reagents

Tetrahydrofuran, dichloromethane and diethyl ether (Aldrich, Lab-Scan, Fluka) were preserved above 4 Å molecular sieves and used without further purification. 1,2,3,4-Tetrahydronaphthalene and quinoline were purified by distillation. Methanesulfonic acid and trifluoromethanesulfonic acid were obtained from Fluka and were used from freshly opened bottles. Deuterated solvents (d-acetone, d-benzene, and d-chloroform) were obtained from Aldrich. Methanol, toluene, 1-methyl-2-pyrrolidinone, acetic acid, 2-propanol, N,N-dimethylformamide, and hexane (Aldrich, Lab-Scan, Fluka AG) were used without purification. Pyridine (Lab-Scan) was preserved above potassium hydroxide. AlCl_3 , TiCl_4 , MgBr_2 , and MgCl_2 were fresh and anhydrous. Polystyrene standards were obtained from Aldrich and polyvinyl pyrrolidone standards from Fluka. Vectra A 950 was obtained from Hoechst Celanese. All other reagents, unless otherwise noted, were from Fluka and were used without further purification.

8.2. Oligomerizations

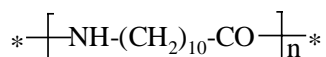
The oligomerizations of 2-alkoxyHBAs were carried out in the presence of p-toluenesulfonyl chloride (TsCl) and N,N-dimethylformamide (DMF) in pyridine (96). The oligomerizations of 2-thioalkoxyHQs and 2-alkoxyHQs were accomplished by the standard solution condensation method by reacting the hydroquinones with terephthaloyl chloride at room temperature in the presence of triethyl amine, Et_3N (97).

The unsubstituted oligoesters used as reference materials were produced by the same procedures as used in the synthesis of substituted oligomers. After oligomerizations the average molecular weights were measured in various solvents with an Ubbelohde-type viscometer or by gel permeation chromatography (GPC). Melting temperatures, T_m , and isotropization temperatures, T_i , of all oligomers were measured by using a polarizing microscope equipped with a hot stage apparatus.

8.3. Blending

All the oligomers were solution blended with PA 11 (*II*) (Fig. 13), where the amount of LC oligomer in the blend was varied from 1 to 50 wt %. The blending of the oligomer with PA 11 was accomplished by dissolving the two compounds in hot 1-methyl-2-pyrrolidinone (NMP). After the polyamide and LC oligomers were completely dissolved they were quantitatively precipitated from excess of methanol. The blends were filtered, extracted 24 hours with methanol, and then dried in a vacuum at 100 °C for several hours.

The ternary blend of oligomer of 2-decanyloxyHBA, Vectra A 950 and PA 11 was prepared by melting a mixture of the three components at 280-300 °C in nitrogen gas atmosphere.



II

Fig. 13. Chemical structure of polyamide 11.

The miscibility of PA 11 with oligomers was studied by DSC and FTIR. In the DSC measurements the point of interest was the melting behavior of the matrix PA 11 phase ($T_m = 189.1$ °C). If there is miscibility the melting point of the crystalline polymer should decrease with increasing content of the second component. Infrared spectroscopy was used to study polymer blend compatibility on a molecular level. The presence of molecular interactions was determined by comparing the spectra of the blends and the spectra of the pure component polymers. Normally differences in the spectra show up as shifts in absorption frequencies, broadening of bands, and changes in the absorptivities of bands of the blended components.

Finally, a three-point bending test was applied to evaluate the differences between flexural properties of blends prepared with various ratios of oligomers and PA 11. The three point bending test was performed without prior processing or orientation of the blends. The samples were compression molded for 10 minutes.

8.4. Instrumentation

^1H NMR spectra were recorded on a Bruker AM 200 MHz or Bruker DPX400 MHz spectrometer in CDCl_3 , d-acetone, or d-benzene. Infrared spectra were measured on a Bruker IFS 66 from KBr pellets. Mass spectra were determined in EI or CI mode with a Kratos MS 80 FF spectrometer. Column chromatography was carried out on silica gel 60 (70-230 mesh, Merck). Thin layer chromatography was performed on 0.25 mm precoated silica gel 60 F_{524} plates (Merck) and the results were viewed by UV light/ I_2 .

The LC phase of oligomers was observed on a Zeiss jenapol polarizing microscope equipped with a Mettler FP 82 hot stage apparatus and a Pentagon 35 mm camera. Molecular weights were determined in THF with a Beckman System Gold HPLC

equipped with Perkin Elmer PL gel $5\mu 10^3 \text{ \AA}$ 0258-2142 column and a UV detector. The polystyrene standards were used for the calibration and the measurements were done at room temperature.

The viscosity measurements were made with an Ubbelohde-type viscometer. The polystyrene and polyvinyl pyrrolidone standards were used as calibration agents.

DSC measurements were performed by using a Mettler TA 3000 DSC20 differential scanning calorimeter in nitrogen gas atmosphere. Samples were first heated from 30 to 250 °C and then allowed to cool to room temperature and heated again to 250 °C. In all cases the heating rate was 10 K/min.

Flexural properties of blends were determined with a 5544 Instron mechanical testing instrument according to SFS 3220/ISO 178 Standard (three-point bending test). The dimensions of test bars were 20 x 2 x 2 mm and the test speed was 5.3 mm/min (**26a-d**, **27-30**), 7.6 mm/min (**26e**) and 5.0 mm/min (**31a-c**, **32a-d**). The length of the span was 16 mm. The conventional deflection was 2.0 (or 3.0) times the thickness of the test bar. σ_b (stress at break) is the stress if the bar is broken before a deflection of 2.0 (or 3.0) times the thickness of the test bar. σ_y (yield stress) is the stress at a deflection equal to 2.0 (or 3.0) times the thickness of the test bar.

9. Results and discussion

9.1. Synthesis of monomers

The monomers used as starting materials in the synthesis of new thermotropic main chain LC oligomers were derivatives of 4-hydroxybenzoic acid (HBA) and hydroquinone (HQ) (Fig. 14).

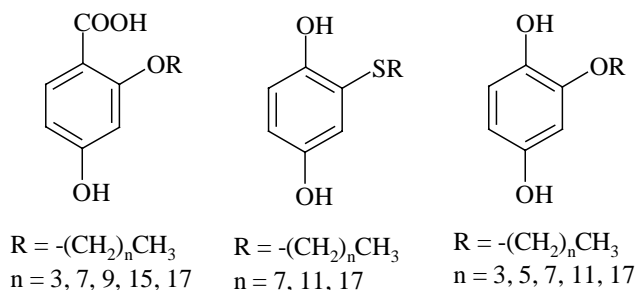


Fig. 14. Chemical structures of 2-alkoxyHBAs, 2-thioalkoxyHQs, and 2-alkoxyHQs.

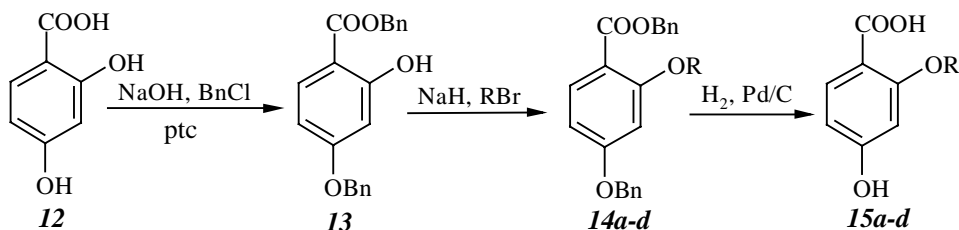
9.1.1. 2-AlkoxyHBAs

Only a few strategies are available for the synthesis of ortho-alkylated 2,4-dihydroxybenzoic acids. A computer-aided literature search utilizing a registry file confirmed that long-chained 2-alkoxy-4-hydroxybenzoic acids (2-alkoxyHBAs) have not been reported previously and their corresponding esters are rare compounds (98-101).

The main feature of the synthesis was the protection of the para-hydroxy group and the carboxyl group of 2,4-dihydroxybenzoic acid with benzyl groups. The protection was easily accomplished in one step from the disodium salt of 2,4-dihydroxybenzoic acid and benzyl chloride without use of any solvents. The ortho-hydroxy group was then alkylated

with sodium hydride and alkyl bromide in the presence of KI and a phase transfer catalyst (ptc) without use of solvent. In the final step, benzyl groups were removed by catalytic hydrogenation to give the target molecules (Scheme 1). The overall yields of the target molecules **15a-d** were 55-75% (Table 1).

The described synthesis serves as a useful route to a variety of 2-alkoxyHBAs. Furthermore, the one-pot protection and solvent-free alkylation makes the method simpler and more general than any of the methods so far described in the literature (III).



RBr = 1-bromobutane (*a*), 1-bromooctane (*b*), 1-bromodecane (*c*),
1-bromooctadecane (*d*)

Scheme 1. Synthetic route for the preparation of 2-alkoxyHBAs.

Table 1. Selected properties of 2-alkoxyHBAs **15a-d** produced by the synthetic route shown in Scheme 1 (III).

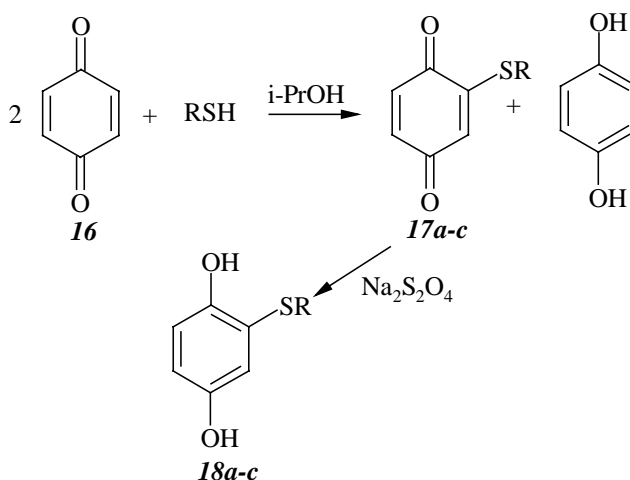
| Compound | Yield (%) | mp (°C) | HRMS | m/z (%), ^a EI, ^b CI |
|------------|-----------|---------|---|--|
| 15a | 56 | 112-113 | C ₁₁ H ₁₄ O ₄ calcd. 210.089 found 210.087 | 210 (11), 154 (12), 136 (100), 110 (25) ^a |
| 15b | 68 | 92 | C ₁₅ H ₂₂ O ₄ calcd. 266.152 found 266.153 | 267 (100), 223 (51), 154 (9), 110 (17) ^b |
| 15c | 76 | 81 | C ₁₇ H ₂₆ O ₄ calcd. 294.183 found 294.182 | 294 (3), 250 (12), 154 (40), 136 (95), 110 (100) ^a |
| 15d | 73 | 91 | C ₂₅ H ₄₂ O ₄ calcd. 406.308 found 406.307 | 362 (8), 110 (100) ^a |

9.1.2. 2-ThioalkoxyHQs

In LC polyesters containing both aromatic diacid and hydroquinone units, substitution in the hydroquinone unit is more effective in T_m reduction than the corresponding

substitution in the diacid moieties (7). Furthermore, in polyesters prepared from alkoxy and alkyl substituted HQs and terephthalic acid the T_m s of the alkoxy substituted compounds have been lower (16). Simple and straightforward routes were therefore sought for the production of thioalkoxy and alkoxy substituted HQs.

2-ThioalkoxyHQs (**18**) were produced almost quantitatively under very mild conditions from 1,4-benzoquinone (BQ) and long chained aliphatic thiols (Scheme 2, Table 2) (I).



RSH = 1-octanethiol (*a*), 1-dodecanethiol (*b*), 1-octadecanethiol (*c*)

Scheme 2. Synthetic route for the preparation of 2-thioalkoxyHQs.

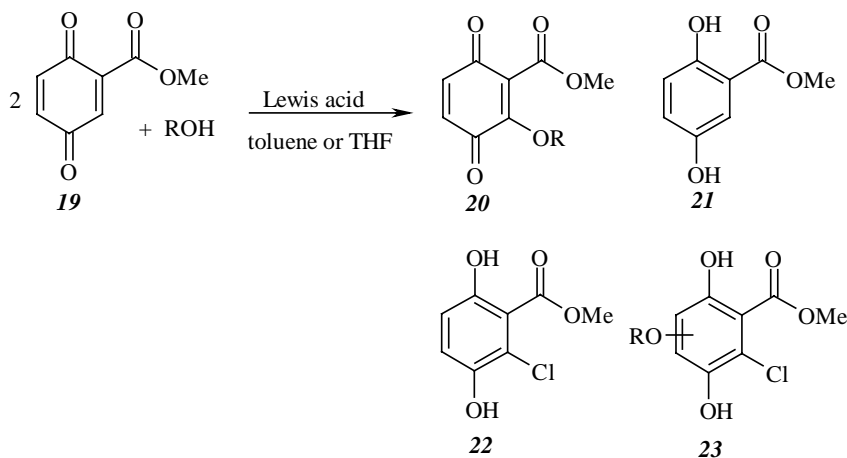
Table 2. Selected properties of 2-thioalkoxyHQs 18a-c produced by the synthetic route shown in Scheme 2 (I).

| Compound | Yield (%) | mp (°C) | HRMS | m/z (%), EI |
|------------|-----------|---------|---|-------------------|
| 18a | 89 | 63 | C ₁₄ H ₂₂ O ₂ S calcd. 254.134 found 254.136 | 254(10), 142(100) |
| 18b | 92 | 76 | C ₁₈ H ₃₀ O ₂ S calcd. 310.197 found 310.195 | 310(12), 142(100) |
| 18c | 95 | 90 | C ₂₄ H ₄₂ O ₂ S calcd. 394.291 found 394.294 | 394(30), 142(100) |

9.1.3. 2-AlkoxyHQs

A synthetic procedure was developed for the preparation of 2-alkoxyhydroquinones. Since a direct addition of alcohol to the BQ did not produce the required monosubstituted product in good yield, several alternative synthetic approaches were tested.

Activated BQ, 2-carbomethoxyBQ (**19**), was chosen as the starting material. The 3-position of **19** possesses a strong electrophilic character and oxygen nucleophiles may attack this position. Initial testing of the addition reaction in the absence of catalyst gave no sign of the desired addition product. Interest was, therefore, next focused on various Lewis acids (LAs) and their ability to catalyze nucleophilic conjugate addition of long chained alcohols to the activated BQ. Several mono- and bidentate LAs in toluene and/or THF in variable molar ratios to the Lewis acid, compound **19**, and 1-octadecanol were tested. The overall results are summarized in Scheme 3 and Table 3.



Scheme 3. Product distribution of Lewis acid catalyzed reaction of 2-carbomethoxyBQ (19**) and 1-octadecanol (ROH).**

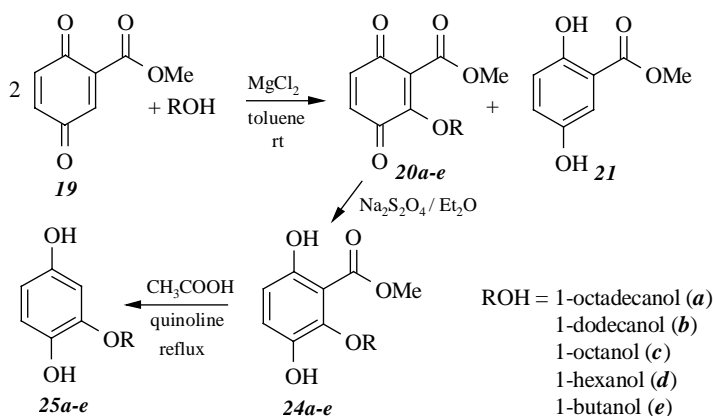
The reactions catalyzed with monodentate AlCl_3 and bidentate TiCl_4 were investigated in more detail by ^1H NMR spectroscopy. Finally anhydrous MgCl_2 was tested as a catalyst for bidentate chelate formation. It was observed that MgCl_2 is an efficient quinone activator towards alcohols both in toluene and in THF. A heterogeneous mechanism of the MgCl_2 catalysis was demonstrated by ^1H NMR spectroscopy.

The reaction of alcohols with 2-carbomethoxy-1,4-BQ (**19**) in the presence of MgCl_2 produced the addition products **20a-e** in 90% yield. These products were reduced to the required HQs **24a-e**, and the methyl ester was cleaved in refluxing quinoline in the presence of acetic acid to give the target hydroquinones **25a-e** in overall yields averaging 45-80% (Scheme 4, Table 4) (II).

Table 3. Product distribution of Lewis acid catalyzed reaction of 2-carbomethoxyBQ (**19**) and 1-octadecanol (ROH).

| Lewis acid [(19):LA:ROH] | Solvent | Products ^a (% yield) | 20 (% yield) |
|--------------------------------------|---------|------------------------------------|------------------------|
| AlCl ₃ (2:1:1) | toluene | 20 (43) | 47 |
| | | 21 (38) ^b | |
| | | 22 (5) | |
| TiCl ₄ (2:1:1) | THF | 21 (19) ^b | - |
| | | 23 (50) | |
| | | 21 (41) ^b | |
| MgBr ₂ (2:1:1) | toluene | 20 (29) | 26 |
| | | 21 (33) | |
| MgCl ₂ (2:1:1) | toluene | | > 90 ^d |
| | | THF | > 90 ^d |
| MgCl ₂ (2:0.01:1) | toluene | | 83 |
| MgCl ₂ (1:1:1) | toluene | | 30 ^e |
| ZnCl ₂ (2:1:1) | toluene | 21 (69) ^b | |
| | | 22 (4) | |
| | | 20 (31) | |
| FeCl ₃ (2:1:1) | THF | 22 (6) | 37 |
| | | 21 (35) ^b | |
| | | 21 (53) ^b | |
| FeCl ₃ (2:1:1) | THF | 20 (30) | 34 |
| | | 21 (46) ^b | |

^a Rest of the reaction mixture contains unidentified polar addition products which were eluted from the column with MeOH. ^b This fraction also contains unreacted alcohol. ^c ¹H NMR and MS spectra of the crude reaction mixture indicated that the major part of the mixture contains reduced starting material **21** and unreacted alcohol and only small amounts of the addition product **20**. ^d According to the ¹H NMR spectrum the only products were **20** and **21**. Product **20** was precipitated from cold methanol. ^e The yield of the product **20** was measured by ¹H NMR.



Scheme 4. Synthetic route for the preparation of 2-alkoxyHQs.

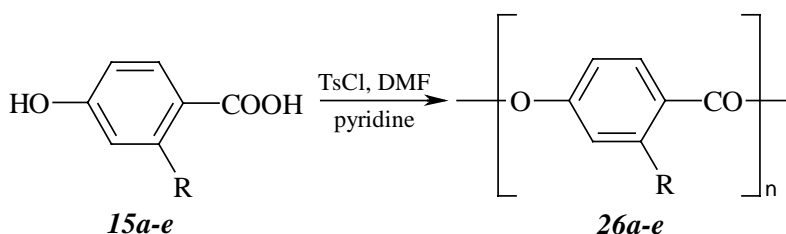
Table 4. Selected properties of 2-alkoxyHQs **25a-e** produced by the synthetic route shown in Scheme 4 (II).

| Compound | Yield (%) | mp (°C) | HRMS | m/z (%), EI |
|------------|-----------|---------|---|---------------------|
| 25a | 81 | 109 | C ₂₄ H ₄₂ O ₃ calcd. 378.313 found 378.316 | 378 (29), 126 (100) |
| 25b | 57 | 100 | C ₁₈ H ₃₀ O ₃ calcd. 294.219 found 294.219 | 294 (9), 126 (100) |
| 25c | 50 | 88 | C ₁₄ H ₂₂ O ₃ calcd. 238.157 found 238.156 | 238 (16), 126 (100) |
| 25d | 50 | 83 | C ₁₂ H ₁₈ O ₃ calcd. 210.126 found 210.127 | 210 (33), 126 (100) |
| 25e | 45 | 79-80 | C ₁₀ H ₁₄ O ₃ calcd. 182.094 found 182.092 | 182 (29), 126 (100) |

9.2. Synthesis of oligomers

9.2.1. Homo-oligomers of 2-alkoxyHBAs

Five new LC homo-oligomers of 2-alkoxyHBAs (**26a-e**) were produced according to the synthesis presented in Scheme 5 (96) (III).



R = -O(CH₂)_xCH₃

x = 3(**a**), 7(**b**), 9(**c**), 17(**d**)

R = H (**e**)

Scheme 5. Oligomerization of 2-alkoxyHBAs **15a-e** in the presence of TsCl and DMF in pyridine.

Average molecular weights (M_v) of homo-oligomers of 2-alkoxyHBAs **26a,b,d** were measured in NMP and tetralin with an Ubbelohde-type viscometer at 93 °C and found to vary between 13 000 and 17 400. Measurements of the homo-oligomers **26a-e** in methanesulfonic acid at 134 °C gave considerably lower M_v s values between 6400 and 9800. A plausible explanation for the lower values may be that methanesulfonic acid reacts much more strongly with the oligomer chains than do NMP and tetralin. In NMP and tetralin the chains of the oligomers seem to exist as dimers (Table 5). A similar dimerization phenomenon was observed in GPC analysis where THF was used as the eluent. For example, M_w of the filtered sample (~70% soluble) of the homo-oligomer of 2-octadecanyloxyHBA (**26d**) was about 11 000.

The interaction between oligomer chains, i.e. self-association, was also observed in their FTIR spectra. Two discrete absorption bands appeared: one at 1725 cm^{-1} which is characteristic of H-bonded carbonyls and the other at 1748 cm^{-1} representing free carbonyl groups. The intensity of the signal of H-bonded carbonyl increased with the decreasing amount of carbon atoms in the side chain of the oligomers. This implies that the main chains of the oligomers have an ability to associate with each other, and the shorter the alkyl chain the better is the association: the oligomer of HBA (**26e**), $C_4 > C_8$, $C_{10} > C_{18}$ (Appendix 1a). Apparently, long side chains in the oligomer inhibit an efficient self-association between the oligomers (22).

Table 5. General properties of homo-oligomers **26a-e** produced by the polycondensation reaction shown in Scheme 5 (III).

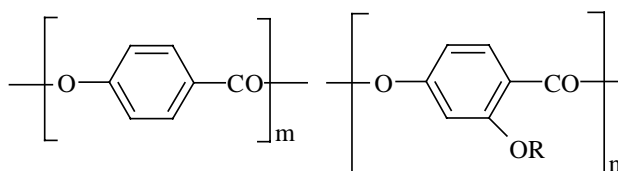
| Oligomer | Yield % | M_v^a | M_v^d | $T_m^e, ^\circ\text{C}$ | $T_i^e, ^\circ\text{C}$ | n |
|------------|---------|---------------------|---------|-------------------------|-------------------------|----|
| 26a | 58 | 14 700 | 8700 | 170 | 230 | 45 |
| 26b | 78 | 13 000 | 6900 | 155 | 197 | 28 |
| 26c | 83 | - ^b | 9800 | 180 | 233 | 36 |
| 26d | 92 | 17 400 ^c | 7700 | 166 | 210 | 20 |
| 26e | 93 | - ^b | 7200 | - ^f | - ^f | 53 |

^a The measurements were made in NMP at 93 °C. ^b A molar mass could not be measured for the products **26c** and **26e** because of their insolubility. However it was assumed that **26c** and **26e** are among the low molecular weight products because the polymerization technique and reaction conditions were the same as in the synthesis of **26a**, **26b**, and **26d**. ^c Measurements were made in 1,2,3,4-tetrahydronaphthalene at 120 °C. ^d Measurements were made in methanesulfonic acid at 134 °C. ^e Melting temperatures (T_m) and isotropization temperatures (T_i) of oligomers **26a-d** were measured by using a polarizing microscope equipped with hot stage. ^f Thermal properties of oligomer **26e** could not be measured due to the limited temperature range of the hot stage (max. temp. 300 °C).

9.2.2. Co-oligomers of 2-alkoxyHBAs and HBA

Random co-oligomers of 2-octanyloxyHBA and HBA (**27**) and 2-hexadecanyloxyHBA and HBA (**28**) were produced. The corresponding block co-oligomers were synthesized from the homo-oligomers of 2-octanyloxyHBA and HBA (**29**) and 2-hexadecanyloxyHBA and HBA (**30**) (Fig. 15). Both the random co-oligomers and the block co-oligomers were prepared under TsCl/pyridine/DMF conditions (96). The

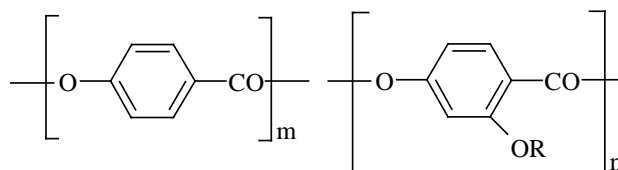
expectation was that these syntheses would produce random co-oligomers where the amounts of aliphatic carbons are approximately the same as in the homo-oligomer of 2-butoxyHBA (**26a**). The effect of the side chain distribution on the final properties of polymer blends could then be studied (IV).



Random co-oligomer of HBA and 2-alkoxyHBA

R = C₈ (**27**), m = 21, n = 27

R = C₁₆ (**28**), m = 38, n = 8



Block co-oligomer of HBA and 2-alkoxyHBA

R = C₈ (**29**), m = 62, n = 28, FTIR; m = 46, n = 21, M_v

R = C₁₆ (**30**), m = 42, n = 18, FTIR; m = 44, n = 18, M_v

Fig. 15. Structures of random and block co-oligomers of HBA and 2-alkoxyHBAs (m and n values are based on FTIR or M_v measurements).

The average molecular weights (M_v) of co-oligomers (**27-30**) were measured in methanesulfonic acid at 134 °C with an Ubbelohde-type viscometer. The amounts of 2-alkoxyHBAs in co-oligomers were determined by FTIR with use of monomeric 2-alkoxyHBAs as calibration agents. The results showed that relative to the homo-oligomer of 2-butoxyHBA (**26a**) (n=45) the amount of aliphatic carbons was slightly larger in the random co-oligomer **27** (n=27) and slightly smaller in the random co-oligomer **28** (n=8). The percentage of 2-alkoxyHBAs in block co-oligomers **29** and **30** was 45 (n=28) and 53 (n=18), respectively. The calculated molecular weights based on FTIR are comparable to the results obtained from the viscosity measurements (Table 6).

It was interesting to note in the case of co-oligomers **27-30** that the intensities of the H-bonded carbonyl signals were increased relative to those of the corresponding homo-oligomers. Apparently, the interactions between the chains are stronger in co-oligomers than in oligomers where alkyl substituents exist regularly in each repeating unit. Comparison of the intensities of H-bonded carbonyl signals of random co-oligomers with the corresponding signals of block co-oligomers showed the interaction between the

chains to be greater in the random co-oligomers. The interactions between the chains of co-oligomers of 2-hexadecanyloxyHBA and HBA (**28**, **30**) are weaker than the corresponding interactions of co-oligomers of 2-octanyloxyHBA and HBA (**27**, **29**), evidently owing to the longer alkyl side chains in the oligomer backbone. The FTIR spectra of co-oligomers **27-30** are presented in Appendix 1b.

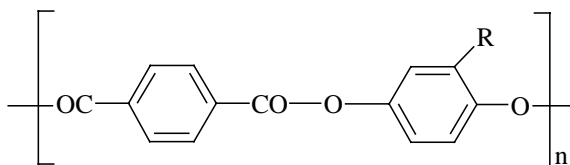
Table 6. General properties of co-oligomers **27-30** produced with the polycondensation reaction shown in Scheme 5 (IV).

| Oligomer | Yield % | M_v^c | % 2-Alkoxy-HBA ^d | T_m^e , °C | T_i^e , °C | m | n |
|-----------------------|---------|---------|-----------------------------|--------------|----------------|-----------------------|-----------------------|
| 27 | 66 | 9500 | 70 | 180 | 260 | 21 | 27 |
| 28 | 70 | 8100 | 37 | 220 | 270 | 38 | 8 |
| 29^a | 59 | 11 400 | 45 | 240 | - ^f | 62, FTIR 46, M_v | 28, FTIR 21, M_v |
| 30^b | 79 | 12 500 | 53 | 165 | 240 | 42, FTIR 44, M_v | 18, FTIR 18, M_v |

^a M_v of homo-oligomer of 2-octanyloxyHBA used in the synthesis of block co-oligomer **29** was 6900. ^b M_v of homo-oligomer of 2-hexadecanyloxyHBA used in the synthesis of block co-oligomer **30** was 6400. ^c Measurements were made in methanesulfonic acid at 134 °C. ^d Composition of the co-oligomers was measured by FTIR with 2-octanyloxyHBA and 2-hexadecanyloxyHBA as calibration agents. ^e Melting temperatures (T_m) and isotropization temperatures (T_i) of oligomers **27-30** were measured with a polarizing microscope equipped with hot stage. ^f T_i of **29** could not be measured due to the limited temperature range of the hot stage (max. temp. 300°C).

9.2.3. Oligomers of terephthaloyl chloride and 2-thioalkoxyHQs

Three LC oligomers of terephthaloyl chloride and 2-thioalkoxyHQs were synthesized (**97**). The structures and properties of oligomers **31a-c** are presented in Fig. 16 and Table 7 (V).



31a-c

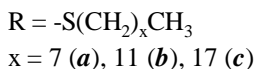


Fig. 16. Structures of oligomers of terephthaloyl chloride and 2-thioalkoxyHQs.

Table 7. General properties of oligomers **31a-c** (V).

| Oligomer | Yield (%) | M_w^a | T_m^c (°C) | T_i^c (°C) |
|------------|-----------|-------------------|--------------|--------------|
| 31a | 67 | 3000 | 240 | 300 |
| 31b | 77 | 4800 | 220 | 300 |
| 31c | 89 | 5100 ^b | 180 | 240 |

^a GPC analysis in THF. Oligomers were soluble only up to 80%. ^b The average molecular weight of oligomer **31c** was measured in trifluoromethanesulfonic acid at room temperature with an Ubbelohde-type viscometer. M_w was then about 3000. ^c Melting temperatures (T_m) and isotropization temperatures (T_i) of oligomers were measured with a polarizing microscope with hot stage.

Carbonyl absorption bands at 1700 cm^{-1} (H-bonded) and $1735\text{-}1740\text{ cm}^{-1}$ (free carbonyl) in the FTIR spectra indicated an interaction between the oligomer chains. The intensity of the carbonyl signal increased with decreasing amount of carbon atoms in the side chain of the oligomers. Again the self-association is directly proportional to the length of the alkyl chains in the oligomers (Appendix 2a).

The viscosity measurements and GPC analysis of **31c** also indicated that the oligomer chains can aggregate (Table 7).

9.2.4. Oligomers of terephthaloyl chloride and 2-alkoxyHQs

Three new LC oligomers of terephthaloyl chloride and 2-alkoxyHQs (**32a-c**), and also unsubstituted poly(1,4-phenyleneterephthalate), were synthesized (**32d**) (97). The structures and properties of the oligomers are presented in Fig. 17 and Table 8 (V).

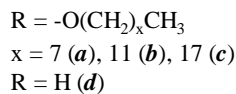
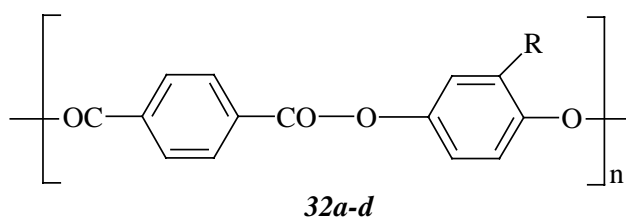


Fig. 17. Structures of oligomers of terephthaloyl chloride and 2-alkoxyHQs (**32a-c**) and terephthaloyl chloride and HQ (**32d**).

Table 8. General properties of oligomers **32a-d** (V).

| Oligomer | Yield (%) | M _w ^a | T _m ^c (°C) | T _i ^c (°C) |
|------------|-----------|-----------------------------|----------------------------------|----------------------------------|
| 32a | 88 | 4300 | 220 | 250 |
| 32b | 70 | 5100 | 210 | 300 |
| 32c | 77 | 9700 | 220 | 280 |
| 32d | 86 | - ^b | - ^d | - ^d |

^a GPC analysis in THF. Oligomers were soluble only up to 80%. ^b A molar mass could not be measured for the product **32d** because of its insolubility. ^c Melting temperatures (T_m) and isotropization temperatures (T_i) of oligomers were measured with a polarizing microscope equipped with hot stage. ^d T_m and T_i of oligomer **32d** could not be measured owing to the limited temperature range of the hot stage (max. temp. 300 °C).

The chains of oligomers prepared from terephthaloyl chloride and 2-alkoxyHQs (**32a-c**) exhibited similar self-association behavior to their sulfur analogues. Again the intensity of the carbonyl signal increased with decreasing amount of carbon atoms in the side chain of the oligomer. The strongest self-association was measured for the oligomer **32d** prepared from terephthaloyl chloride and HQ. The FTIR spectra are given in Appendix 2b.

It was interesting to note that the intensities of the H-bonded carbonyl signals of oligomers of 2-alkoxyHBAs are much stronger than those of oligomers **31a-c** and **32a-c**. Apparently, the self-associations are greater in the series of oligomers of 2-alkoxyHBAs and HBA than in the series of oligomers of terephthaloyl chloride and thioalkoxy or alkoxyHQs.

9.3. Preparation and properties of blends

9.3.1. PA 11 and homo-oligomers of 2-alkoxyHBAs

Melting temperatures of PA 11/oligomer blends varied with the amount of LC oligomer **26a-e** in the blend. The measurements revealed that oligomers containing 4 to 10 carbon atoms in the side chain have adhesion towards PA 11. The melting temperatures of the blends decreased with increasing amount of oligomer **26a-c** in the blend. In contrast to this, the oligomer **26d**, which has a very long side chain (C₁₈), had little effect on the melting point of the polyamide even when the concentration was increased to 50%. A similar result was obtained for the wholly aromatic oligomer **26e**: only a slight decrease was noticed in T_m of PA 11. The only small decreases in T_m of PA 11 implied that the oligomers **26d** and **26e** are only partially compatible with the polyamide (Fig. 18). A plausible explanation for the immiscibility of oligomer **26d** might be the long alkyl chains, which by increasing free volume of the oligomer chains cause a decrease in the electronic interactions between the oligomer and PA 11. In turn the wholly aromatic nature of the oligomer **26e** increases the interfacial tension between the LCP and PA 11 and reduces the adhesion (III).

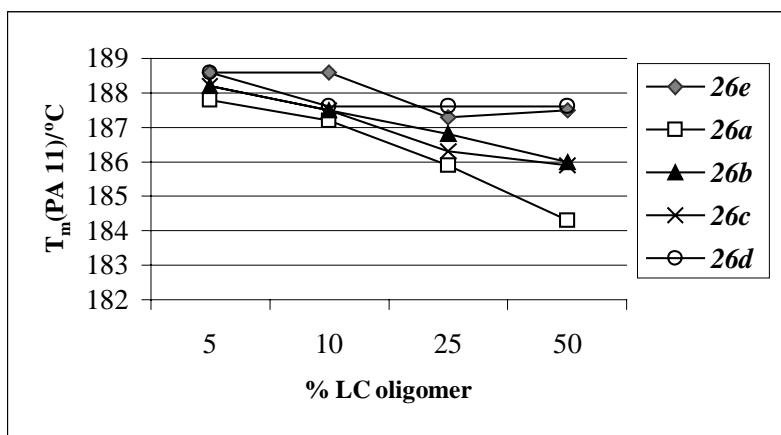


Fig. 18. Melting temperature of PA 11 in PA 11/26a-e blends as a function of LC oligomer content [T_m (PA 11)= 189.1 °C].

FTIR analysis of the homo-oligomers was focused on the frequency at 1190 cm^{-1} (-C-O stretching), where the spectral differences were clearest. The absorption frequency shifts downwards with increasing amount of oligomer **26a-d** in the blend, which supports the existence of interactions between the blended compounds. The shifts in signals were greater for the blends of oligomers **26a-c**. In fact, no frequency shifts at all were observed for blends of the oligomer **26d** until the concentration in the blend reached 50 wt %. The blends of PA 11 and **26e** gave only sum spectra of the pure compounds. The FTIR spectra are presented in Appendixes 3 and 4.

In a three-point bending test all oligomers **26a-e** were unexpectedly found to strengthen the polyamide matrix. The flexural properties of the polyamide were improved by the addition of just 1% of LC homo-oligomer. The stress values decreased with increasing amount of oligomer in the blend (Table 9).

The results presented in Table 9 show that the stress values of 1 wt % blends decreased with increasing amount of aliphatic carbons in the oligomer structure. The result can be explained in terms of self-association of the oligomer chains, the degree of which is directly proportional to the length of the alkyl chains in the homo-oligomers. The shorter the alkyl side chain in the homo-oligomer the stronger is its self-association and the better its strengthening ability. Evidently the oligomers have reached their critical molar mass through intramolecular interactions and possess some polymer-like properties.

Table 9. Stress values of PA 11^a/26a-e oligomer blends (III).

| Oligomer | wt % | Stress ^b (σ) (MPa) | Stress ^c (σ) (MPa) | Oligomer | wt % | Stress ^b (σ) (MPa) | Stress ^c (σ) (MPa) |
|------------|------|---|---|------------|------|---|---|
| 26a | 1 | 88 (σ_y) | 81 (σ_y) | 26d | 1 | 78 (σ_y) | 74 (σ_y) |
| | 5 | 70 (σ_b) | 68 (σ_y) | | 5 | 44 (σ_b) | 44 (σ_b) |
| | 10 | 47 (σ_b) | 47 (σ_b) | | 10 | 33 (σ_b) | 33 (σ_b) |
| 26b | 1 | 83 (σ_y) | 78 (σ_y) | 26e | 1 | 89 (σ_b) | 76 (σ_y) |
| | 5 | 76 (σ_b) | 76 (σ_b) | | 5 | 74 (σ_b) | 74 (σ_b) |
| | 10 | 60 (σ_b) | 60 (σ_b) | | 10 | 60 (σ_b) | 60 (σ_b) |
| 26c | 1 | 84 (σ_y) | 78 (σ_y) | | | | |
| | 5 | 67 (σ_b) | 67 (σ_b) | | | | |
| | 10 | 58 (σ_b) | 58 (σ_b) | | | | |

^a σ_y (PA 11) = 63 MPa. ^b The conventional deflection is 3.0 times the thickness of the test bar. σ_b (stress at break) is the stress if the bar was broken before a deflection of 3.0 times the thickness of the test bar. σ_y (yield stress) is the stress at a deflection equal to 3.0 times the thickness of the test bar. ^c The conventional deflection is 2.0 times the thickness of the test bar.

9.3.2. PA 11 and co-oligomers of 2-alkoxyHBAs and HBA

Co-oligomers of 2-alkoxyHBAs and HBA 27-30 were found to depress slightly the melting temperature of PA 11 in PA 11/co-oligomer blends. The greatest T_m depression was measured for the random co-oligomer of 2-hexadecanyloxyHBA and HBA (28) (Fig. 19). The results indicate stronger adhesion of the random co-oligomers than the block co-oligomers to the aliphatic polyamide. The weaker adhesion of the block co-oligomers may be due to the incorporation of more aromatic dispersed parts in the block co-oligomers ($m = 62$ (29), 42(30)) than in the corresponding random co-oligomers ($m = 21$ (27), 38(28)). Large amounts of wholly aromatic parts reduce the adhesion by increasing the interfacial tension.

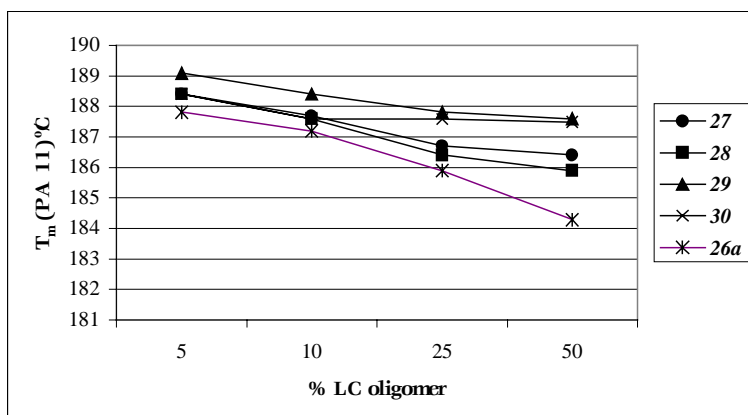


Fig. 19. Melting temperature of PA 11 in PA 11/27-30, 26a blends as a function of LC oligomer content [T_m (PA 11) = 189.1 °C].

The miscibility of both random and block co-oligomers was poorer than the miscibility of the corresponding homo-oligomers of 2-alkoxyHBA where the amount of aliphatic carbons is approximately the same. For instance, the greatest T_m decreases of homo-oligomer of 2-butoxyHBA and co-oligomer of 2-hexadecanyloxyHBA and HBA in their 50% blends were 4.8 and 3.2 °C, respectively (IV).

In the FTIR study, attention was focused on the wavenumbers between 1160 cm^{-1} and 1050 cm^{-1} (-C-O stretching). The absorption frequency shifts downwards with increasing amount of co-oligomer in the blends. The shift supports the existence of interactions between the blended compounds. The frequency shifts were slightly greater in the blends of random co-oligomers than in the blends of block co-oligomers. The FTIR spectra are presented in Appendixes 5 and 6.

The flexural properties of PA 11 were improved upon the addition of co-oligomers, with the greatest enhancement in strength achieved through the addition of just 1% of co-oligomer (Table 10).

Table 10. Stress values of PA 11^a/LC co-oligomer **27-30** blends (IV).

| Oligomer | wt % | Stress ^b (σ) (MPa) | Stress ^c (σ) (MPa) | Oligomer | wt % | Stress ^b (σ) (MPa) | Stress ^c (σ) (MPa) |
|-----------|------|---|---|-----------|------|---|---|
| 27 | 1 | 89 (σ_b) | 86 (σ_y) | 29 | 1 | 84 (σ_y) | 80 (σ_y) |
| | 5 | 65 (σ_b) | 65 (σ_b) | | 5 | 62 (σ_b) | 62 (σ_b) |
| | 10 | 59 (σ_b) | 59 (σ_b) | | 10 | 60 (σ_b) | 60 (σ_b) |
| 28 | 1 | 93 (σ_b) | 87 (σ_y) | 30 | 1 | 82 (σ_y) | 78 (σ_y) |
| | 5 | 74 (σ_b) | 74 (σ_b) | | 5 | 72 (σ_b) | 72 (σ_b) |
| | 10 | 60 (σ_b) | 60 (σ_b) | | 10 | 51 (σ_b) | 51 (σ_b) |

^a σ_y (PA 11) = 63 MPa. ^b The conventional deflection is 3.0 times the thickness of the test bar. σ_b (stress at break) is the stress if the bar was broken before a deflection of 3.0 times the thickness of the test bar. σ_y (yield stress) is the stress at a deflection equal to 3.0 times the thickness of the test bar. ^c The conventional deflection is 2.0 times the thickness of the test bar.

The flexural properties of 1 wt % blends of homo- and co-oligomers of 2-alkoxyHBAs and HBA were compared. The strengths of the blends of random co-oligomers **27** and **28** and homo-oligomers of 2-butoxyHBA (**26a**) and HBA (**26e**) are 89, 93, 88, 89 MPa, respectively. In comparison, the strengths of the blends of block co-oligomers **29** and **30** and homo-oligomers of 2-octanyloxyHBA (**26b**) and 2-decanyloxyHBA (**26c**) are 84, 81, 83, and 84 MPa, respectively. The least strengthening of all was observed for the homo-oligomer of 2-octadecanyloxyHBA (**26d**), 78 MPa. These results show that the final mechanical properties of the blend are directly proportional to the total amount of aliphatic carbons in the alkyl side chains of the oligomer. The strengthening ability of the oligomer increases as the total amount of aliphatic carbons in the side chains decreases.

The stress values show that the length of alkyl side chain has no direct effect on flexural properties of blends. For instance, the stress values of the 1 wt % blends of random co-oligomer of 2-hexadecanyloxyHBA and HBA (**28**) and homo-oligomer of 2-octadecanyloxyHBA (**26d**) are 93 and 78 MPa, respectively.

9.3.3. PA 11 and oligomers of terephthaloyl chloride and 2-thioalkoxyHQs and 2-alkoxyHQs

The DSC results revealed poor adhesion between PA 11 and oligomers synthesized from terephthaloyl chloride and 2-thioalkoxyHQs (**31a-c**) and from terephthaloyl chloride and 2-alkoxyHQs (**32a-d**). The melting temperature of PA 11 (189.1 °C) remained almost unaffected even when the oligomer content was increased to 50 wt % (Table 11). The FTIR spectra, which are collected in Appendixes 7,8, and 9, support the DSC results (V).

Table 11. Melting temperatures of PA 11 in PA 11/LC oligomer **31a-c**, **32a-d** blends (V).

| Oligomer | wt % | T _m (PA 11) / °C | Oligomer | wt % | T _m (PA 11) / °C |
|------------|------|-----------------------------|------------|------|-----------------------------|
| 31a | 10 | 189.1 | 32a | 10 | 189.1 |
| | 25 | 189.0 | | 25 | 188.4 |
| | 50 | 188.4 | | 50 | 188.0 |
| 31b | 10 | 189.5 | 32b | 10 | 188.0 |
| | 25 | 189.1 | | 25 | 188.6 |
| | 50 | 188.8 | | 50 | 188.4 |
| 31c | 10 | 189.0 | 32c | 10 | 188.0 |
| | 25 | 188.2 | | 25 | 189.2 |
| | 50 | 188.0 | | 50 | 189.1 |
| | | | 32d | 10 | 189.8 |
| | | | | 25 | 189.0 |
| | | | | 50 | 189.2 |

Results of a three-point bending test showed that the oligomers **31a-c** and **32a-d** could strengthen the polyamide matrix (Table 12).

Table 12. Stress values of PA 11^a /LC oligomer **31a-c**, **32a-d** blends (V).

| Oligomer | wt % | Stress ^b (σ) (MPa) | Oligomer | wt % | Stress ^b (σ) (MPa) |
|------------|------|-------------------------------|------------|------|-------------------------------|
| 31a | 1 | 71 (σ _y) | 32a | 1 | 72 (σ _y) |
| | 5 | 65 (σ _y) | | 5 | 71 (σ _y) |
| | 10 | 58 (σ _b) | | 10 | 71 (σ _y) |
| 31b | 1 | 66 (σ _y) | 32b | 1 | 67 (σ _y) |
| | 5 | 64 (σ _y) | | 5 | 65 (σ _y) |
| | 10 | 67 (σ _b) | | 10 | 60 (σ _y) |
| 31c | 1 | 56 (σ _y) | 32c | 1 | 66 (σ _y) |
| | 5 | 54 (σ _y) | | 5 | 68 (σ _y) |
| | 10 | 56 (σ _y) | | 10 | 66 (σ _b) |
| | | | 32d | 1 | 78 (σ _y) |
| | | | | 5 | 77 (σ _b) |
| | | | | 10 | 64 (σ _b) |

^a σ_y (PA 11) = 63 MPa. ^b The conventional deflection is 2.0 times the thickness of the test bar. σ_b (stress at break) is the stress if the bar was broken before a deflection of 2.0 times the thickness of the test bar. σ_y (yield stress) is the stress at a deflection equal to 2.0 times the thickness of the test bar.

The results showed that a slight enhancement in the flexural properties of PA 11 was achieved by adding even 1% of oligomers **31a-b** and **32a-d** to the matrix. The oligomer **31c** was the only compound that did not strengthen PA 11.

It is interesting to note once again that the yield stress values of oligomers with the same amount of aliphatic carbons in the side chain are closely similar. The strengths of the 1 wt % blends of unsubstituted oligomer of terephthaloyl chloride and HQ (**32d**), S_8 (**31a**), O_8 (**32a**), S_{12} , (**31b**), O_{12} (**32b**), S_{18} (**31c**), O_{18} (**32c**) were 78, 71, 72, 66, 67, 56, 66 MPa respectively. The only exception was oligomer **31c**, which did not strengthen PA 11 similarly to **32c**. A plausible explanation is that the average molecular weight of **31c** is only half that of **32c**. In addition, the long side chain in **31c** inhibits an efficient self-association of the oligomer chains. These two strength-diminishing features together result in a low strength blend.

The results described show that the main chains of the oligomers have the ability to associate. The shorter the alkyl side chain the better is the association. The interactions between the chains of co-oligomers of 2-alkoxyHBAs **27-30** were stronger than those of the corresponding homo-oligomers **26a-d**. The self-association of random co-oligomers **27, 28** was greater than that of the block co-oligomers **29, 30**. The strongest H-bonded carbonyl signal was measured for unsubstituted oligomer of HBA (**26e**).

According to the FTIR results the ability of homo- and co-oligomers of 2-alkoxyHBAs to self-associate is as follows: unsubstituted oligomer of HBA (**26e**) > random C_8 (**27**) > block C_8 (**29**) > random C_{16} (**28**) > block C_{16} (**30**) > C_4 (**26a**) > C_8 (**26b**) > C_{10} (**26c**) > C_{18} (**26d**). The self-association of the oligomers of terephthaloyl chloride and 2-thioalkoxyHQs and of terephthaloyl chloride and 2-alkoxyHQs is also better for the oligomers with short alkyl side chains. The order was the following: unsubstituted oligomer of terephthaloyl chloride and HQ (**32d**) > S_8 (**31a**) > O_8 (**32a**) > S_{12} , O_{12} (**31b**, **32b**) > S_{18} , O_{18} (**31c**, **32c**). The degree of self-association in this series was systematically lower than in the series of oligomers of 2-alkoxyHBAs.

The miscibility of the blended compounds was characterized by DSC and FTIR. T_m depressions and spectral differences showed the tendency of the LC oligomers of 2-alkoxyHBAs to interact with PA 11 to be as follows: C_4 (**26a**) > random C_{16} (**28**), random C_8 (**27**), C_{10} (**26c**), C_8 (**26b**) > block C_8 (**28**), block C_{16} (**30**), unsubstituted oligomer of HBA (**26e**), C_{18} (**26d**).

Blending of the oligomers of terephthaloyl chloride and 2-thioalkoxyHQs or 2-alkoxyHQs with PA 11 did not decrease the melting temperature of PA 11. The DSC data implied that the interactions of the oligomers **31a-c** and **32a-d** with PA 11 were weak. FTIR analysis supported the DSC results: no clear differences between the spectra of the blends and those of the component polymers were detected.

A three-point bending test was used to evaluate the differences between blends prepared with various ratios of oligomer to PA 11. Blending of oligomers **26a-e**, **31a,b**, and **32a-d** with PA 11 improved the flexural properties of the polyamide. The greatest enhancement was achieved through addition of just 1% of LC oligomer. A plausible explanation for the enhancement is that the oligomer chains are able to self-associate and take on some polymer-like properties. The results show that the final mechanical properties of the matrix polymer are directly related to the total amount of aliphatic carbons in the alkyl side chains of the oligomers.

The stress values of 1 wt % blends of oligomers of HBAs and terephthaloyl chloride and HQs given above are not directly comparable owing to the different ways of

measuring the parameters. The conventional deflection in the case of oligomers of HBAs is 3.0 times the thickness of the test bar, while for oligomers of terephthaloyl chloride and HQs the corresponding deflection is 2.0 times the thickness of the test bar. The stress values of 2.0 x deflection of unsubstituted oligomer of HBA (**26e**), randomC₈ (**27**), randomC₁₆ (**28**), blockC₈ (**29**), blockC₁₆ (**30**), C₄ (**26a**), C₈ (**26b**), C₁₀ (**26c**), C₁₈ (**26d**) are 76, 86, 87, 80, 78, 81, 78, 78 and 74 MPa, respectively (Tables 9 and 10). The results indicate that the yield stress values of oligomers produced from terephthaloyl chloride and 2-thioalkoxyHQs or 2-alkoxyHQs are lower than the corresponding values of oligomers of 2-alkoxyHBAs. The lower yield stress values are partly due to the poorer self-association of the oligomers **31a-c** and **31a-d** than the oligomers of 2-alkoxyHBAs.

9.3.4. Oligomer of 2-decanyloxyHBA as a compatibilizer in LCP/PA 11 blend

As a final step, it was interesting to know if the oligomers of 2-alkoxyHBAs might have a role as compatibilizers in immiscible LCP/thermoplastic blends. The oligomer of 2-decanyloxyHBA (**26c**) was tested as a compatibilizer for the blend of LCP (Vectra A 950) and PA 11. As can be seen from the DSC results in Table 13, the melting point of PA 11 ($T_m = 189.1$) is clearly depressed by the addition of oligomer **26c** to the LCP/PA 11 blend. Evidently the oligomer **26c** has a good compatibilizing effect, enhancing the interfacial adhesion between aliphatic PA 11 and wholly aromatic LCP.

Table 13. Melting temperatures of PA 11 in the blends of PA 11 + oligomer 26c, PA 11 + LCP, and PA 11 + LCP + oligomer 26c. LCP is Vectra A 950 [T_m (PA 11) = 189.1 °C].

| blends | T_m (PA 11) / °C |
|--|--------------------|
| PA 11 + oligomer 26c (90/10) | 187.5 |
| PA 11 + LCP (80/20) | 189.0 |
| PA 11 + LCP + oligomer 26c (72/14/14) | 179.0 |

10. Conclusions

Polymer blends of LCP and thermoplastic matrix have been studied intensively during recent years. As has often been demonstrated, the addition of small amounts of LCP to a thermoplastic polymer can result in significant changes in processability and mechanical properties.

However, wholly aromatic LCPs are incompatible with the majority of the available commercial thermoplastics. The properties of the blends, and particularly the impact strength, are poorer than expected on the basis of the additivity rule. Compatibilization is then necessary to enhance the adhesion between the phases.

Novel synthetic routes were developed for the preparation of monomers 2-alkoxyHBAs **15a-d** and 2-alkoxyHQs **25a-e** and a larger-scale process was developed for the preparation of 2-thioalkoxyHQs **18a-c**. The monomers, with alkyl chains as their side chain substituents, were utilized in the synthesis of novel liquid crystalline oligomers **26a-d**, **27-30**, **31a-c**, and **32a-c**, and the oligomers were then blended with aliphatic PA 11. The adhesion between the blended compounds and the ability of the oligomeric LC compounds to enhance the flexural properties of the polyamide were studied.

Miscibility studies showed the homo-oligomer of 2-butoxyHBA to have strongest interactions with PA 11. Unsubstituted wholly aromatic oligomers, homo-oligomer of 2-octadecanyloxyHBA, and oligomers of terephthaloyl chloride and 2-thioalkoxyHQs/2-alkoxyHQs resulted in blends with considerably weaker adhesion between aliphatic PA 11 and the oligomer.

The results also showed that the strengthening ability of an oligomer is directly proportional to the total amount of aliphatic carbons. The best strengthening was obtained with unsubstituted oligomers, random co-oligomers, and homo-oligomer of 2-butoxyHBA.

The results obtained demonstrated the effect of the amount of aliphatic carbons and their distribution in the LC oligomer backbone on the miscibility of an LC oligomer with an aliphatic polymer. Furthermore, they demonstrate the ability of LC oligomers to strengthen PA 11 if their self-association is efficient enough.

Preliminary DSC investigations of a ternary blend of the homo-oligomer of 2-decanyloxyHBA, PA 11, and Vectra A 950 revealed the compatibilizing effect of the oligomer. Apparently, this oligomer is able to enhance the interfacial adhesion between PA 11 and Vectra A 950. In the future, LC oligomers of 2-alkoxyHBAs might well become important components in the design of new generation compatibilizers.

11. References

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