Unexpected Strengthening of Polyamide 11 with Liquid Crystalline Oligomers of 2-Alkoxy-4-hydroxybenzoic Acids. 1

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Received April 23, 1998; Revised Manuscript Received September 3, 1998

ABSTRACT: Novel liquid crystalline (LC) oligomers of 2-alkoxy-4-hydroxybenzoic acids (**5a**−**d**) containing flexible side chains were produced, and their compatibilities with polyamide 11 (PA 11) were investigated. DSC and FTIR studies revealed variable interfacial adhesion between blended compounds. They indicated that oligomers with short or medium long alkoxy substituents (**5a**−**c**) have adhesion to PA 11 while the interactions between oligomers of 4-hydroxybenzoic acid (**5e**) or 2-octadecanyloxy-4-hydroxybenzoic acid (**5d**) and PA 11 were poor. FTIR spectra proved that oligomeric structures could self-associate and affect on the final mechanical properties of the polyamide. Strength of PA 11 in a three point bending test was increased by addition of only 1% of LC oligomers **5a**−**e** to the matrix.

Introduction

Polymer blends containing liquid crystalline polymers (LCPs) and thermoplastic matrixes have received considerable attention during recent years. Blending offers a means for exploiting the good properties of thermotropic main chain LCPs in tailoring the properties of thermoplastic for different applications.[2] The addition of small amounts of an LCP to a thermoplastic polymer can result in significant reform in processability and mechanical properties. The great improvement in tensile properties is due to the formation of fibrillar structure of LCP in the matrix and the strong interfacial adhesion between the two polymers.[3]

Unfortunately the majority of the available commercial thermoplastics are incompatible with wholly aromatic LCPs, and the properties of blends are then lower than expected on the basis of the additivity rule. Compatibilization is then necessary to enhance the adhesion between two phases. The addition of compatibilizing agents into intrinsically immiscible polymer blends gives substantial help in solving the problems of poor dispersion and low adhesion. The location of a compatibilizer at the phase interfaces reduces interfacial tension, resulting in improved blend component dispersion with adhesion between the blend phases. The compatibilizers are normally low molecular weight compounds or oligomers that possess lower melting temperatures relative to the base polymers. Also monomeric multifunctional compounds have been demonstrated to be highly effective couplers in polymer blends.[4]

However, the compatibilization process itself can present difficulties. Most of the compatibilized LCP blends tend to hinder LCP fibril formation and therefore reduce the mechanical properties of the final material. To solve this problem the use of LC materials as compatibilizers in the thermoplastic/LCP blends have attracted considerable attention in recent years.[5] The LCP compatibilizer can prevent the rupture of fibrillar LCP phase, and the fibrils can then act as reinforcing elements.

The ultimate purpose of our research is to find new oligomeric LC compounds with flexible spacers attached to the polymer as a substituent which improves the interaction between aliphatic and aromatic polymers. In this paper, we have concentrated on studies of adhesion between various LC oligomers and aliphatic PA 11 and the ability of oligomeric LC compounds to enhance the flexural properties of the polyamide.[6]

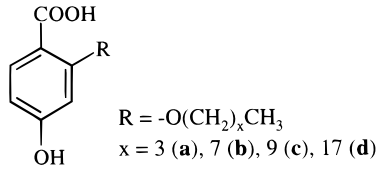


Figure 1.

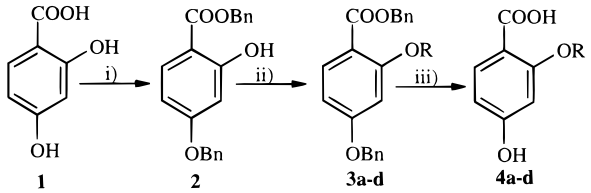
We have synthesized a series of new LC oligomers of 2-alkoxy-4-hydroxybenzoic acids (**5a**−**d**) which have variable adhesion to PA 11 and could surprisingly reinforce the polyamide without any processing or orientation prior to the bending test.

Results and Discussion

Monomer Syntheses. 4-Hydroxybenzoic acids are interesting starting materials for the syntheses of commercially important LCPs. We describe here an efficient synthesis of 2-alkoxy-4-hydroxybenzoic acids (**4a**−**d**) (Figure 1, Scheme 1, Table 1 and 2) and their application in the synthesis of new main chain LC oligomers.[7]

Oligomer Syntheses. Oligomers of 2-alkoxy-4-hydroxybenzoic acids (**5a**−**d**) and 4-hydroxybenzoic acid (**5e**) were produced by using a direct polycondensation of **4a**−**d** and 4-hydroxybenzoic acid in pyridine in the

Scheme 1



i) NaOH, BnCl, ptc.; ii) NaH, RBr; iii) H_2, Pd/C
RBr = a) 1-bromobutane, b) 1-bromooctane, c) 1-bromodecane, d) 1-bromooctadecane

10.1021/ma980660c CCC: $15.00
Published on Web 11/07/1998

Table 1. Selected Data of Benzyl 2-Alkoxy-4-benzyloxybenzoates (3a−d)

compound	yield (%)	HRMS	*m/z* (%)	^{1}H-NMR δ (ppm)
3a	76[a]	$C_{25}H_{26}O_4$: calcd 390.183, found 390.181	390 (7), 91 (100)[c]	0.90 (t, 3H), 1.46 (m, 2H), 1.70 (m, 2H), 4.03 (t, 2H), 5.19 (s, 2H), 5.28 (s, 2H), 6.65 (dd, 1H, J = 8.6, 2.4 Hz), 6.71 (d, 1H, J = 2.2 Hz), 7.35−7.46 (m, 10 H), 7.81 (d, 1H, J = 8.6 Hz)
3b	84[a]	$C_{29}H_{34}O_4$: calcd 446.246, found 446.247	446 (4), 91 (100)[c]	0.88, 1.28 (10H), 4.02, 5.17, 5.30, 6.65 (8.6, 2.4 Hz), 6.71 (2.1 Hz), 7.35−7.47, 7.83 (8.6 Hz)
3c	94[a]	$C_{31}H_{38}O_4$: calcd 474.277, found 474.277	475 (20), 367 (22), 91 (100)[d]	0.88, 1.28 (14H), 1.75, 4.03, 5.18, 5.30, 6.68, 7.36−7.50, 7.83 (8.5 Hz)
3d	89[b]	$C_{39}H_{54}O_4$: calcd. 586.402, found 586.402	586 (1), 91 (100)[d]	0.87, 1.28 (30H), 1.75, 4.03, 5.19, 5.29, 6.65 (8.6, 2.3 Hz), 6.71 (2.1 Hz), 7.35−7.50, 7.81 (8.6 Hz)

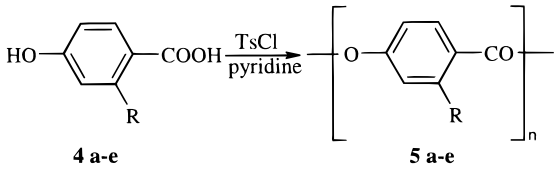
[a] Crude. [b] Isolated, mp. 58 °C. [c] EI. [d] CI.

Table 2. Selected Data of 2-Alkoxy-4-hydroxybenzoic Acids (4a−d)

compound	yield (%)	mp (°C)	HRMS	*m/z* (%)	^{1}H-NMR δ (ppm)
4a	90	112−113	$C_{11}H_{14}O_4$: calcd 210.089, found 210.087	210 (11), 154 (12), 136 (100), 110 (25)[a]	0.99, 1.53 (m, 2H), 1.85, 4.24, 6.57 (8.6, 2.2 Hz), 6.64 (2.2 Hz), 7.86 (8.6 Hz)
4b	94	92	$C_{15}H_{22}O_4$: calcd. 266.152, found 266.153	267 (100), 223 (51), 154 (9), 110 (17)[b]	0.87, 1.28 (10H), 1.85, 4.24, 6.58 (8.6, 2.3 Hz), 6.64 (2.1 Hz), 7.86 (8.6 Hz)
4c	92	81	$C_{17}H_{26}O_4$: calcd 294.183, found 294.182	294 (3), 250 (12), 154 (40), 136 (95), 110 (100)[a]	0.87, 1.28 (14H), 1.85, 4.24, 6.58 (8.6, 2.3 Hz), 6.64 (2.1 Hz), 7.86 (8.6 Hz)
4d	94	91	$C_{25}H_{42}O_4$: calcd 406.308, found 406.307	362 (8), 110 (100)[a]	0.87, 1.28 (30H), 1.86, 4.23, 6.57 (8.5, 2.1 Hz), 6.62 (2.0 Hz), 7.85 (8.5 Hz)

[a] EI. [b] CI.

Scheme 2



4 a-e **5 a-e**

R = -O(CH$_2$)$_x$CH$_3$
x = 3 (**a**), 7 (**b**), 9 (**c**), 17 (**d**)
R = H (**e**)

Table 3. General Properties of Oligomers 5a−e

oligomer	yield (%)	M_v	T_m[d] (°C)	T_i[d] (°C)
5a	58	14 700[a]	170	230
5b	78	13 000[a]	155	197
5c	83	*b*	180	233
5d	92	17 400[c]	166	210
5e	93	*b*	*e*	*e*

[a] The measurements were made in NMP at 93 °C. [b] We could not measure a molar mass for the products **5c** and **5e** because of their insolubility. However we assumed that **5c** and **5e** belong also to the low molecular weight products because we used the same polymerization technique and the reaction conditions as in the synthesis of **5a**, **5b**, and **5d**. [c] The measurements were made in tetralin at 120 °C. [d] Melting temperatures (T_m) and isotropization temperatures (T_i) of oligomers **5a−d** were measured by using polarizing microscope equipped with hot stage. [e] Thermal properties of oligomer **5e** could not be measured due to the limited temperature range of hot stage (maximum temperature 300 °C).

presence of *p*-toluenesulfonyl chloride (TsCl) and *N,N*-dimethylformamide (DMF)[9] (Scheme 2 and Table 3).

After oligomerizations we first measured the average molecular weights of LC products in 1-methyl-2-pyrrolidinone (NMP) or 1,2,3,4-tetrahydronaphthalene (tetralin) by using an Ubbelohde-type viscometer. These measurements implied that all the products from polycondensation reactions were oligomeric (Table 3).[10]

FTIR Analysis. Oligomers. We found from the FTIR spectra of **5a−e** that there were two discrete absorption bands at 1725 and 1748 cm^{-1}. The former signal is characteristic for H-bonded carbonyls, and the latter, for free carbonyl groups.[11] In our case the intensity of the H-bonded carbonyl increases with a decreasing amount of carbon atoms in the side chain of oligomers. It implies that the main chains of oligomers have the ability to associate with each other, and the shorter the alkyl chain the better is the association. Apparently the associated oligomers have then, some properties of polymers. Recent publications in the literature have demonstrated that rigid rod polymers based on monosubstituted building blocks tend to form sanidic layer structures and so-called double stacks.[12] They also revealed that the strength of the electronic interactions between the main chains play an important role in the final macroscopic properties of polymers. These observations also support our results that the oligomers **5a−e**, which are composed of monosubstituted monomers, have the ability to self-associate and that the oligomers with shorter side chains form bigger aggregates than the oligomers substituted with long alkyl chains.

Blends of PA 11 and 5a−e. Infrared spectroscopy has been used to study polymer blend compatibility on a molecular level. In the present work, the presence of molecular interactions have been determined by examining the differences between the spectra of the blends and the spectra of the component polymers. Normally these spectral differences include shifts in the absorption frequency, broadening of the bandwidth, and changes in the absorptivity of the bands.[13]

Furthermore, we could not detect any polyester−polyamide copolymer formation through an ester−amide interchange reaction, which is typically observed in the catalyzed melt processes of polyesters and polyamides.[6d]

FTIR analyses have been focused on the frequency at 1190 cm^{-1} where the spectral differences were most clearest. The absorption frequency shifts with increasing amount of oligomers **5a−d** in the blends, which supports the existence of interactions between the blended compounds. The shifts of signals were greater in the blends of oligomers **5a−c** where smaller amounts of the oligomer in the blend (10 and 25 wt %) caused

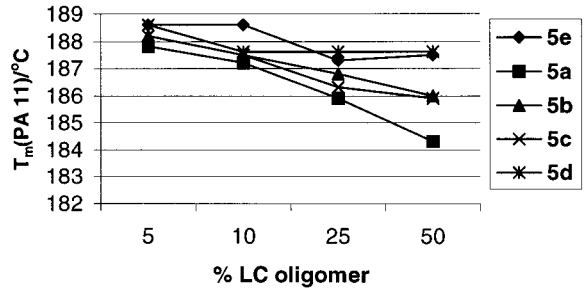


Figure 2. Melting temperature of PA 11 in the PA 11/**5a**−**e** blends vs LC oligomer content.

Table 4. Stress Values of PA 11[a]/5a−e Oligomer Blends

oligomer	wt %	stress,[b] (σ_b, σ_y) (MPa)	oligomer	wt %	stress,[b] (σ_b, σ_y) (MPa)
5a	1	88 (σ_y)	**5d**	1	78 (σ_y)
	5	70 (σ_b)		5	44 (σ_b)
	10	47 (σ_b)		10	33 (σ_b)
5b	1	83 (σ_y)	**5e**	1	89 (σ_b)
	5	76 (σ_b)		5	74 (σ_b)
	10	60 (σ_b)		10	60 (σ_b)
5c	1	84 (σ_y)			
	5	67 (σ_b)			
	10	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.

greater frequency shifts than in the blends of the oligomer **5d** where a clear frequency shift can be seen only in the 50 wt % blend.

The blends of PA 11 and **5e** gave only sum spectra of pure compounds and gave more evidence about their immiscibility.

Differential Scanning Calorimetry. In DSC measurements our interest was focused on the behavior of the matrix PA 11 phase. The most important information obtained from the DSC curves was the melting behavior of PA 11. It was noted that the melting temperatures of PA 11 (T_m = 189.1 °C) in the blends apparently decrease with addition of LC oligomers to the system (Figure 2). These DSC measurements revealed that oligomers **5a**−**c**, which contain 4−10 carbon atoms in the side chain, have adhesion to PA 11. Maximum T_m decreases of oligomers **5a**, **5b** and **5c** were 4.8, 3.1, and 3.2 °C, respectively. On the other hand in the case of **5d** with very long (18 carbons) side chain and of the wholly aromatic oligomer, **5e**, the T_m of PA 11 was nearly constant even when the oligomer content was increased (maximum T_m decreases: 1.5 (**5d**) and 1.6 °C (**5e**)). Only slight decreases in melting point of polyamide implied that the oligomers **5d** and **5e** are only partially compatible with the polyamide. A plausible explanation for the immiscibility of oligomer **5d** might be the increasing free volume due to the long alkyl chains which decreases the electronic interactions between **5d** and PA 11.[12a] On the other hand the wholly aromatic chemical nature of the oligomer **5e** increases the interfacial tension to aliphatic polyamide and reduces the adhesion.[3c]

Mechanical Testing. A three-point bending test was used for evaluation of differences between blends prepared from various ratios of oligomers **5a**−**e** in PA 11 (Table 4). The results surprisingly showed that the enhancement of the flexural properties of PA 11 were achieved by addition of only small amounts of oligomeric LC materials (**5a**−**e**) to the matrix. We found for example that the stress values of 1 wt % PA 11 blends with oligomers **5e**, **5a**, **5b**, **5c**, and **5d** are 89, 88, 83, 84, and 78 MPa, respectively. This implies that the flexural properties are directly proportional to the length of the alkyl chains in the oligomers. This phenomenon can be explained by the oligomer association discussed earlier.[14] Apparently the long side chains in the oligomer inhibit an efficient self-association between the oligomer chains. It seems that oligomers have reached their critical molar mass by intramolecular interactions and can improve the strengths of PA 11 blends without any processing or orientation.[15]

Conclusion

In this study we have developed an efficient three step synthetic route to produce 2-alkoxy-4-hydroxybenzoic acids (**4a**−**d**) for the syntheses of novel LC oligomers (**5a**−**d**). The oligomers **5a**−**e** were blended with PA 11, and a clear interaction between compounds **5a**−**c** and the polyamide was observed by using DSC and FTIR. The compatibilities of **5d**,**e** and the aliphatic polyamide were weaker. The flexural properties of polyamide were improved by addition of only 1% of LC oligomers to the PA 11. The improvement of the flexural properties is directly proportional to the length of the alkyl chains in the oligomers: C_0, $C_4 > C_8$, $C_{10} > C_{18}$. Apparently the long side chains in the oligomer inhibit an efficient self-association between the oligomer chains.

Experimental Section

The LC phase of oligomers were observed on a Zeiss jenapol polarizing microscope equipped with a Mettler FP 82 hot stage apparatus and a Pentagon 35 mm camera.

The viscosity measurements were made with an Ubbelohde-type viscometer below T_m at 93 °C in NMP or at 120 °C in tetralin. The polystyrene standards (M_w = 2360, 3700, 12860, and 18700) were used as calibration agents. The flow rates of each sample (30.0 mg/10 mL) were measured five times and the averaged flow rates were used in the final calculations. The average molecular weights of oligomers were determined from the calibration curve ($R^2 > 0.95$) of polystyrene standards.

DSC measurements were performed on a Mettler TA 3000 DSC20 differential scanning calorimetry in a nitrogen gas atmosphere. All the blend samples were first heated from 30 to 250 °C and then allowed to cool to room temperature and heated again to 250 °C. A heating rate of 10 K/min was used at all cases.

Infrared spectra were performed as KBr pellets using a Bruker IFS 66 spectrometer.

Flexural properties of blends were determined in Engineering Mechanics Laboratory at the University of Oulu according to SFS 3220/ISO 178 Standard by a three point bending test. The dimensions of test bars were 20 × 2 × 2 mm and the test speed was 5.3 mm/min (**5a**−**d**) and 7.6 mm/min (**5e**). The length of the span was 16 mm. The conventional deflection in the present work 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.

Melting points are reported uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM 200 MHz spectrometer in acetone-*d*. Infrared spectra were performed on a Bruker IFS 66 spectrometer using KBr pellets and CCl_4 samples. Mass spectra were determined on a Kratos MS 80FF spectrometer by the EI and CI mode. Thin-layer chromatography was performed on 0.25 mm precoated silica gel 60 F_{254} and viewed by UV light/I_2. The yields are not optimized.

Benzyl 4-Benzyloxy-2-hydroxybenzoate (2). 2,4-Dihydroxybenzoic acid (**1**) (200 g, 1.30 mol) and 2 equiv of NaOH (103.82 g, 2.60 mol) were mixed in 600 mL of methanol. After 30 min of mixing, methanol was evaporated to dryness. Disodium salt of 2,4-dihydroxybenzoic acid (**1**) was treated with benzyl chloride in the presence of catalytic amount of ptc (~0.5 g, tetrabutylammonium bromide). The reaction was carried out under a nitrogen gas atmosphere at 150 °C, until TLC indicated that benzyl chloride had reacted completely. R_f (benzyl chloride) = 0.92, R_f(**1**) = 0.16, R_f(**2**) = 0.86 (eluent: 40% EtOAc/hexane). The reaction mixture was extracted with Et_2O and H_2O. The organic layer was dried and evaporated. The product was isolated from methanol to give a 90% (390.53 g, 1.17 mol) yield of white crystalline product (**2**). Characterization: mp 87 °C; IR (KBr) 3180, 3000−2800, 1680, 1620, 1260, 1150, 1000 cm^{-1}; ^1H NMR (200 MHz, acetone-*d*) δ 5.19 (s, 2H), 5.40 (s, 2H), 6.60 (m, 1H), 7.36−7.50 (m, 10H), 7.81 (d, 1H, J = 1.7 Hz), 10.95 (s, 1H); MS m/z (%) + EI M^+ 334 (36), 225 (3), 110 (100); HRMS, EI calcd for $C_{21}H_{18}O_4$ 334.120, found 334.123.

General Procedure for the Preparation of Benzyl 2-Alkoxy-4-Benzyloxybenzoates (3a−d). Benzyl 2-octadecanyloxy-4-benzyloxybenzoate (3d). Benzyl 4-benzyloxy-2-hydroxybenzoate (**2**) (50.0 g, 0.15 mol) was first mixed with 1.1 equiv of 55% NaH (7.18 g, 0.30 mol) in 400 mL of THF. Organic solvent was evaporated and the sodium salt of **2** was allowed to react with 1.2 equiv of 1-bromooctadecane (59.82 g, 0.18 mol) in the presence of catalytic amounts of KI and ptc (~0.1 g, tetrabutylammonium bromide). The reaction mixture was heated to 120 °C and mixed for 2 days without solvent. The mixture was cooled to room temperature and extracted with diluted HCl and Et_2O. The organic layer was dried and concentrated under reduced pressure. The product was recrystallized from methanol and the yield of **3d** was 89% (78.0 g, 0.13 mol). Characterization: mp. 58 °C; IR (KBr) 3150−3000, 3000−2850, 1680, 1620, 1450, 1250, 1150, 1000, 750 cm^{-1}; ^1H NMR (200 MHz, acetone-*d*): δ 0.87 (t, 3H), 1.28 (s, 30H), 1.75 (m, 2H), 4.03 (t, 2H), 5.19 (s, 2H), 5.29 (s, 2H), 6.65 (dd, 1H, J = 8.6, 2.3 Hz), 6.71 (d, 1H, J = 2.1 Hz), 7.35−7.50 (m, 10 H), 7.81 (d, 1H, J = 8.6 Hz); MS m/z (%) + CI, M^+ 586 (1), 91 (100); HRMS, EI calcd for $C_{39}H_{54}O_4$ 586.402, found 586.402.

Benzyl 2-butoxy-4-benzyloxybenzoate (**3a**), benzyl 2-octanyloxy-4-benzyloxybenzoate (**3b**), and benzyl 2-decanyloxy-4-benzyloxybenzoate (**3c**) were prepared using the same procedure (Table 1), and they were used as crude products in the following debenzylation step.

General Procedure for the Preparation of 2-Alkoxy-4-hydroxybenzoic Acids (4a−d). 2-Octadecanyloxy-4-hydroxybenzoic Acid (4d). Benzyl 2-octadecanyloxy-4-benzyloxybenzoate (**3d**) (10 g, 17 mmol) and an equivalent weight of 10% Pd/C were suspended in 250 mL of EtOAc. The mixture was stirred under 90−100 bar of hydrogen until debenzylation had completed. The reaction mixture was filtered and removal of solvent under reduced pressure yielded 94% (6.5 g, 16 mmol) of the final target molecule **4d**. Characterization: mp 91 °C; IR (KBr) 3250, 3000−2850, 1700, 1620, 1450, 1260, 1050, 750 cm^{-1}; ^1H NMR (200 MHz, acetone-*d*) δ 0.87 (t, 3H), 1.28 (m, 30H), 1.86 (m, 2H), 4.23 (t, 2H), 6.57 (dd, 1H, J = 8.5, 2.1 Hz), 6.62 (d, 1H, J = 2.0 Hz), 7.85 (d, 1H, J = 8.5 Hz); MS m/z (%) + EI 362 (8), 110 (100); HRMS, CI calcd for $C_{25}H_{42}O_4$ 406.308, found 406.307.

2-Butoxy-4-hydroxybenzoic acid (**4a**), 2-octanyloxy-4-hydroxybenzoic acid (**4b**), and 2-decanyloxy-4-hydroxybenzoic acid (**4c**) were prepared using the same procedure (Table 2).

General Procedure for the Preparation of Oligomers of 2-Alkoxy-4-hydroxybenzoic Acids and Oligomer of 4-Hydroxybenzoic Acid (5a−e). Oligomer of 2-octadecanyloxy-4-hydroxybenzoic acid (5d). A solution of TsCl (9.40 g, 49 mmol) and DMF (0.83 g, 11 mmol) in 40 mL of pyridine was maintained at room temperature for 30 min. 2-Octadecanyloxy-4-hydroxybenzoic acid (**4d**) (7.70 g, 19 mmol) dissolved in 40 mL of pyridine was then added to the reaction mixture. The mixture was maintained at room temperature for about 15 min and then at 120 °C for 4−5 h. The reaction mixture was poured into methanol and the precipitated product was isolated by filtration. The oligomer of 2-octadecanyloxy-4-hydroxybenzoic acid (**5d**) was purified with Soxhlet extraction using methanol as a solvent and finally evaporated to dryness. The yield of **5d** was 92% (6.8 g).

Oligomers of 2-butoxy-4-hydroxybenzoic acid (**5a**), 2-octanyloxy-4-hydroxybenzoic acid (**5b**), and 2-decanyloxy-4-hydroxybenzoic (**5c**) acid and oligomer of 4-hydroxybenzoic acid (**5e**) were produced by using the same method (Table 3).

Blending. Oligomers **5a**−**e** were solution blended with PA 11 and the amount of LC oligomer in the blends were varied from 1 to 50 wt %. The blending of PA 11 and LC oligomers was carried out by dissolving the both compounds in hot NMP. After the polyamide and LC oligomers were completely dissolved they were quantitatively precipitated from excess of methanol. The blends were filtered and extracted 24 h with methanol and after that dried in a vacuum at 100 °C for several hours.

Acknowledgment. This research was supported financially by the Neste Oy Foundation. We thank Mrs. Paivi Joensuu (University of Oulu) for mass spectra and Mr. Kalle Vahataini (Engineering Mechanics Laboratory, University of Oulu) for the three-point bending test analysis. Also Sari Hyvarinen (University of Helsinki, Laboratory of Polymer Chemistry) is acknowledged for guidance in microscopic measurements.

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(1) The monomer syntheses procedure is extracted from the MSc thesis of K.A.T.

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(7) Only a few strategies are available for the synthesis of *ortho* alkylated 2,4-dihydroxybenzoic acid.[8] A computer-aided literature search by utilizing registry file confirmed that long chained 2-alkoxy-4-hydroxybenzoic acids have not been reported previously and their corresponding esters are rare compounds. Our simple synthesis of the 2-alkoxy-4-hydroxybenzoic acid monomers is outlined in Scheme 1. The preparation of the dibenzylated product involved the formation of the disodium salt of 2,4-dihydroxy benzoic acid. In the next step sodium salt was mixed with benzyl chloride in the presence of a phase transfer catalyst (ptc) (tetrabutylammo-

nium bromide) without any solvent at 150 °C. The yield of the dibenzylation was about 90%. The dibenzylated product was then treated with sodium hydride and finally the sodium salts of **2** were treated with 1-alkylbromides (1-bromobutane, 1-bromooctane, 1-bromodecane, and 1-bromooctadecane) in the presence of KI and ptc. The yields of the alkylations averaged 76−94%. The final step in the synthetic sequence was an exhaustive debenzylation which was performed by using Pd/C catalyst under 90−100 bar hydrogen pressure. The synthesis described here serves as a useful route to a variety of 2-alkoxy-4-hydroxybenzoic acids (**4a**−**d**) in good overall yields. Furthermore, one-pot protection and solvent-free alkylation makes the method more general and simple than the previous examples in the literature.

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MA980660C