

FTIR and strengthening studies on liquid crystalline oligomers of 2-thioalkoxy/2-alkoxyhydroquinones and terephthaloyl chloride

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Abstract

The properties of liquid crystalline (LC) oligomers produced from 2-thioalkoxyhydroquinones (2-thioalkoxyHQs) and 2-alkoxyhydroquinones (2-alkoxyHQs) with terephthaloyl chloride (**1a–c**, **2a–c**) have been studied and their compatibility with polyamide 11 (PA 11) has been investigated. FTIR studies showed two conformations of the synthesized oligomers. A three-point bending test indicated that oligomeric chains could strengthen the final flexural properties of the polyamide. Strength of PA 11 was increased by addition of only 1% of LC oligomers to the matrix. Compatibility between oligomer chains and PA 11 was lower than the compatibility between corresponding oligomers of 2-alkoxy-4-hydroxybenzoic acids (2-alkoxyHBAs) and PA 11. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In LCP/thermoplastic blends the major direction of research is towards compatibilizers or third components to improve the interaction between the components. The interaction between blend components can also be improved by modifying the blend components [1,2].

We have recently studied new main chain liquid crystalline homo- and co-oligomers of 2-alkoxyHBA and HBA containing variable length of alkoxy side chains (0–18) and their blends with PA 11 [3,4]. We showed then the results from FTIR studies about the structural and conformational changes of the oligomers and the ability of oligomers to enhance the final flexural properties of PA 11.

Since oligomers of 2-alkoxyHBA could strengthen the PA 11 matrix we were next interested to know if similar behavior and properties could be observed also in the case of other typical LCPs, such as poly(1,4-phenyleneterephthalate)s, with flexible side chains. In the present study we have produced LC oligomers by using thioalkoxyHQs and terephthaloyl chloride (**1a–c**) as starting materials and compared their properties with oligoesters prepared from alkoxy substituted HQs and terephthaloyl chloride (**2a–c**)

(Fig. 1). The corresponding unsubstituted oligoester (**3**) was also produced and applied as a reference material.

2. Results and discussion

2.1. Characterization of oligomers

The molecular weight distributions summarized in Table 1 were measured by GPC with THF as a solvent and polystyrene as standards. The data gives a somewhat lower estimate of the molecular weight as the oligomers were soluble in THF only up to 80% under the applied conditions. The number average molecular weights, M_n , varied between 1400 and 4400 g/mol, and the weight average molecular weights, M_w , varied between 3000 and 9700 g/mol, which can be seen as typical numbers for polyesters made by solution polycondensation. The distributions were monomodal and the polydispersities ranged between 1.5 and 2.2. The GPC shows that oligomers were indeed formed in the solution polycondensation.

Here, infrared spectroscopy was utilized to study structural and conformational behavior of the oligomers. Previously, Kolodyazhnyi et al. [5] have used dipole-moment measurements in the investigation of conformations of various *para* and *ortho* substituted phenyl

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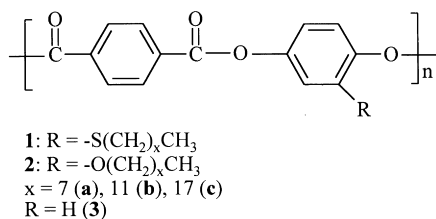


Fig. 1. Structures of oligomers of terephthaloyl chloride and 2-thioalkoxyHQs (**1a–c**) or 2-alkoxyHQs (**2a–c**) and oligomer of terephthaloyl chloride and HQ (**3**).

benzoates. Their results showed that *ortho* substituted phenyl benzoates can have conformations presented in Fig. 2. The conformation A was preferred when measurement was made in a nonpolar solvent such as benzene.

In infrared spectra polar substituents in the *ortho*-position can split C=O and C=C bands due to groups in different environments. In our previous study alkoxy substituent in *ortho*-position of aromatic ring splitted C=O and C=C bands in infrared spectra due to two different rotational isomers of the oligomers [4,6]. In the present study two carbonyl signals were also noticed at wavenumbers 1740 and 1700 cm^{-1} which indicates the existence conformations A and B of the oligomers, respectively (Figs. 3 and 4). The intensity of signal at 1700 cm^{-1} is directly proportional to the amount of aliphatic carbons in the alkyl side chains of the oligomer. It seems that the existence of the conformation B slightly increases as the amount of aliphatic carbons in the side chain decreases. Apparently, a long alkyl substituent

prevents an efficient rotation about C(Ar)–O–C(carbonyl) bonds.

In this context we applied one monomeric compound, 2-methoxyphenyl benzoate, as a reference material and compared its FTIR spectrum with the spectra of oligomers. In the spectrum of the 2-methoxyphenyl benzoate there were also two carbonyl bands at wavenumbers 1733 and 1694 cm^{-1} which indicate the existence of the two isomers.

The thermal properties of the oligomers are shown in Table 2. Phase transition temperatures were determined using DSC up to 300°C and the results from the second heating were used. The oligomers exhibited distinct endothermal melting transitions between 240 and 180°C. The oligomers **1c** and **2c** had also a transition around 40–60°C which was obviously due to the melting of the substituent. The other oligomers exhibited a similar transition in the first heating run, but it could not be seen in the following heating run. To detect the LC behavior the oligomers were studied by light microscopy between crossed polarizers. All oligomers exhibited a liquid crystalline behavior above the melting point. Birefringent textures could be seen, and the oligomers flowed very easily upon shearing. Nematic textures were then obtained after annealing for several hours above the melting point. The isotropization temperature varied between 240 and 300°C. Upon further heating decomposition starts to occur.

2.2. Characterization of blends

A three-point bending test was used to evaluate the differences between blends prepared with various ratios of LC oligomer in PA 11. The results showed that the enhancement of the flexural properties of PA 11 were already achieved by addition of only 1% of oligomers **1a–b**, **2a–c** and **3** to the matrix (Table 3). The oligomer **1c** was the only compound which did not strengthen PA 11.

A plausible explanation for the enhancement of the flexural properties of PA 11 is that the oligomer chains are able to interact and take on some polymer-like properties. In our previous study the interaction between oligomer chains were noticed by comparing the viscosity measurements made in 1-methyl-2-pyrrolidinone (NMP) and 1,2,3,4-tetrahydronaphthalene (tetralin) with the measurements made in methanesulfonic acid [3,4]. Then the average molecular weights (M_v) were clearly lower in methanesulfonic acid than in NMP and tetralin. The observed reduction in M_v in acidic solvent may be caused by the fact that the solvent used interacts much stronger with the oligomer

Table 1

Yields and molecular weights of the synthesized oligomers **1a–c**, **2a–c** and **3**

Oligomer	yield (%)	M_n^a	M_w^a	D
1a	67	1400	3000	2.2
1b	77	3200	4800	1.5
1c^b	89	3000	5100	1.7
2a	88	2600	4300	1.7
2b	70	3500	5100	1.5
2c	77	4400	9700	2.2
3	86	– ^c	–	–

^a Analyzed by GPC in THF. Oligomers were soluble only up to 80%.

^b Viscosity measurement of oligomer **1c** in trifluoromethanesulfonic acid at room temperature gave ~ 3000 as M_v .

^c A molar mass could not be measured for the product **3** because of its insolubility.

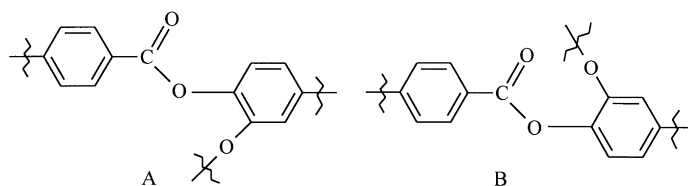


Fig. 2. Rotational isomers (A, B) of oligomers of terephthaloyl chloride and thioalkoxy or alkoxy substituted HQs.

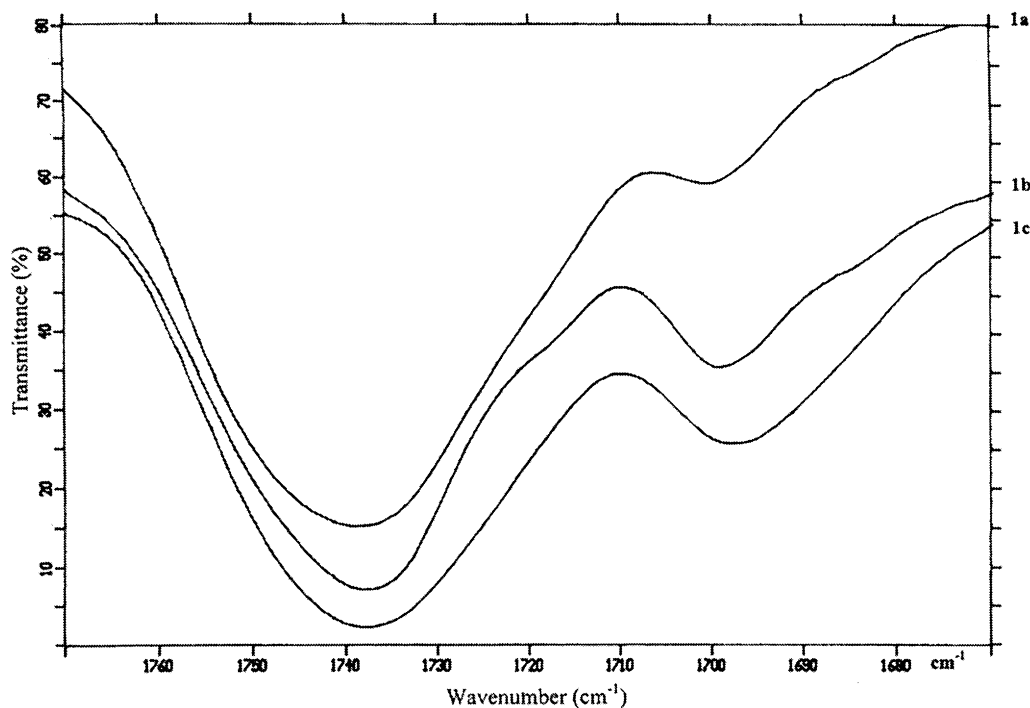


Fig. 3. FTIR spectra of oligomers **1a–c** in the region of 1770–1670 cm^{-1} .

chains and can disperse the molecular interactions while in NMP and tetralin the oligomer chains can interact and the chains exist as dimers. In the present study a similar dimerization phenomenon was observed in the viscosity measurement of oligomer **1c**. The molecular weight of **1c** in trifluoromethanesulfonic acid was about 3000 g/mol while

in GPC analysis in THF the corresponding value was about 5000 g/mol.

Although the viscosity measurements indicate that oligomer chains are able to interact and own some properties of polymers the yield stress values of oligomers **1a–b**, **2a–c** and **3** were lower than the corresponding values of

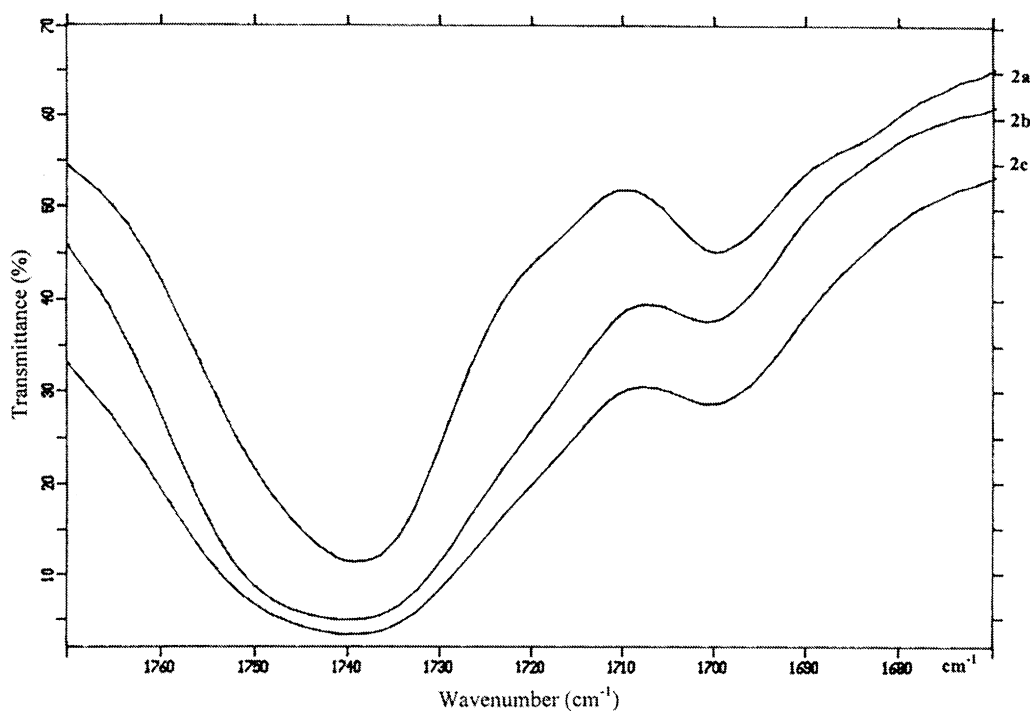


Fig. 4. FTIR spectra of oligomers **2a–c** in the region of 1770–1670 cm^{-1} .

Table 2
Thermal properties of the synthesized oligomers **1a–c**, **2a–c** and **3**

Oligomer	T_m^a (alkyl substituents) (°C)	T_m^a (oligomers) (°C)	T_{n-i}^a (isotropization temperature) (°C)
1a	–	240	300
1b	–	220	300
1c	40	180	240
2a	–	220	250
2b	–	210	300
2c	60	220	280

^a Melting temperatures (T_m) of alkyl substituents and oligomers, and isotropization temperatures (T_{n-i}) of oligomers were obtained by DSC.

oligomers of 2-alkoxyHBAs [3,4]. The results from three-point bending test indicate clear differences in strengthening ability between oligomers of 2-alkoxyHBAs and the oligomers of terephthaloyl chloride and 2-thioalkoxy/2-alkoxyHQs. The conventional deflection was always twice the thickness of the test bar in the case of terephthaloyl derivatives, since the maximum stress value was obtained already then. On the other hand in the case of oligomers of 2-alkoxyHBAs the stress value increased even clearly after a deflection of twice the thickness.

It seems that the chains in the HBA based oligomers are more rigid than in the oligomers of terephthaloyl chloride and 2-thioalkoxy/2-alkoxyHQs precisely as in the case of corresponding polyamides, poly(*p*-benzamide) and poly-(1,4-phenylene terephthalamide). More rigid structures of the oligomers of 2-alkoxyHBAs strengthen PA 11 matrix more efficiently than do the corresponding terephthaloyl derivatives and higher stress values were obtained in the three-point bending test [7].

It is interesting to note that the yield stress values of oligomers with same amount of aliphatic carbons in the side chain (**1a**, **2a** and **1b**, **2b**) are quite similar. The only exception was the oligomer **1c** which could not strengthen PA 11 similarly as **2c**. A plausible explanation is that the average molecular weight of **1c** is only half of the corresponding value of **2c** together with that the long side

Table 3
Stress values of PA 11/LC oligomer blends (σ_y (PA 11) = 63 MPa)

Oligomer	Wt.%	Stress (MPa)	Oligomer	Wt.%	Stress (MPa)
1a	1	71(σ_y)	2a	1	72(σ_y)
	5	65(σ_y)		5	71(σ_y)
	10	58(σ_b)		10	71(σ_y)
1b	1	66(σ_y)	2b	1	67(σ_y)
	5	64(σ_y)		5	65(σ_y)
	10	67(σ_b)		10	60(σ_y)
1c	1	56(σ_y)	2c	1	66(σ_y)
	5	54(σ_y)		5	68(σ_y)
	10	56(σ_y)		10	66(σ_b)
			3	1	78(σ_y)
				5	77(σ_b)
				10	64(σ_b)

Table 4
Melting temperatures of PA 11 in the PA 11/LC oligomer blends (T_m (PA 11) = 189.1°C)

Oligomer	Wt.%	T_m (PA 11) (°C)	Oligomer	Wt.%	T_m (PA 11) (°C)
1a	10	189.1	2a	10	189.1
	25	189.0		25	189.1
	50	188.4		50	188.4
1b	10	189.5	2b	10	188.0
	25	189.1		25	188.0
	50	188.8		50	188.6
1c	10	189.0	2c	10	188.4
	25	188.2		25	188.0
	50	188.0		50	189.2
			3	10	189.1
				25	189.8
				50	189.0
					189.2

chains in the oligomer inhibit an efficient interaction between the oligomer chains.

In DSC measurements our interest was focused on the melting behavior of the matrix PA 11 phase. It was noted that the melting temperatures of PA 11 in the blends did not decrease with addition of LC oligomers **1a–c**, **2a–c** and **3** to the system (Table 4). These DSC measurements revealed that the compatibility of compounds **1a–c**, **2a–c** and **3** with PA 11 is poor [8,9]. The results show that the compatibility of oligomers **1a–c**, **2a–c** and **3** with PA 11 is lower than the compatibility between previously studied oligomers of 2-alkoxyHBAs with PA 11. For example maximum T_m decrease of oligomer of 2-butoxyHBA is 4.8°C, while the corresponding value of oligomer **2a** is only 1.1°C.

Infrared spectroscopy has been used to study polymer blend compatibility on a molecular level. The differences between the spectra of the blends and the spectra of the component polymers implied the possible interaction between blended compounds. In the miscible blend system the absorption frequency shifts with increasing amount of the other component in the blends which supports the existence of interactions between the blended compounds [10]. In our case the blends of PA 11 and **1a–c**, **2a–c** and **3** gave only sum spectra of pure compounds which implied their poor miscibility. FTIR analysis supports DSC results which also indicated poor compatibility between PA 11 and LC oligomers.

In our previous studies of homo- and co-oligomers of 2-alkoxyHBAs the existence of adhesion between blended compounds were noticed by absorption frequency shifts [3,4]. For example, the frequency shift in a 50% blend of 2-butoxyHBA in PA 11 was about 3 cm⁻¹.

3. Experimental section

3.1. Materials

Terephthaloyl chloride, HQ and triethylamine from

Aldrich (99%) were used as received without further purification. Tetrahydrofuran (Prolab, pro analysi) was dried over calcium hydride and distilled. 2-ThiooctanyloxyHQ, 2-thiododecanyloxyHQ, 2-thiooctadecanyloxyHQ, 2-octanyloxyHQ, 2-dodecanyloxyHQ and 2-octadecanyloxyHQ were synthesized according to the recently published methods [11,12].

3.2. Oligomerizations

Two groups of oligoesters (**1a–b**, **2a–c**) with thioalkoxy respective alkoxy substituents were synthesized. The oligomerization was done by the standard solution condensation method by reacting the HQ with terephthaloyl chloride at room temperature in the presence of triethyl amine. Five mmol of the HQ was weighed into a 100 ml flask under nitrogen. The flask was sealed with a septum, and then 10 mmol triethyl amine in 20 ml dry THF was added with a syringe. After the dissolution of the HQ, 5 mmol of terephthaloyl chloride diluted in 20 ml dry THF was added dropwise with a syringe. The solution was vigorously mixed during the addition of the acid chloride. The flask was then left under mixing for 24 h. As a reference, an oligoester without any alkyl substituents (**3**) was synthesized similarly from terephthaloyl chloride and HQ.

The resulted oligomers were isolated by precipitation from cold ethanol and filtrated. The precipitate was washed with water to remove residual triethylamine salt and dried.

3.3. Characterization of oligomers

Number- and weight-average molecular weights were determined in THF with a Millipore Waters 200 HPLC equipped with four Ultrastaygel columns (10⁴, 1000, 500 and 100 Å) and a RI detector. Polystyrene standards were used for the calibration and the measurements were done at room temperature. The viscosities of oligomer solutions were first measured with an Ubbelohde viscometer at 115°C in a mixture of ethanolamine/NMP (4:1 by volume). However a sudden drop in viscosity indicated the degradation of oligomer chains in the ethanolamine/NMP mixture. Previous studies have implied that some aromatic polyesters are soluble in sulfonic acid solvents [13]. In the present study trifluoromethanesulfonic acid was tested as a solvent in viscosity measurements. Apparently, oligomer chains did not degrade in the applied solvent during measurement, since no sudden drops in viscosity were noticed. Therefore the final measurements were done at room temperature in trifluoromethanesulfonic acid. The polyvinyl pyrrolidone standards ($M_w = 10\,000, 24\,000, 44\,000; 20.0\text{ mg}/10\text{ ml}$) were used as the calibration agents. The flow rates of each sample were measured three times and the averaged flow rates were used in the final calculations. The average molecular weight of oligomer **1c** were determined from the calibration curve ($R^2 > 0.95$) of the polyvinyl pyrrolidone standards.

DSC measurements were done with a Mettler TA 30

differential scanning calorimetry. The thermal analysis was done under nitrogen and with a heating rate of 10 K/min. For the DSC measurements the samples were heated from 0 to 300°C, then quickly cooled to down to 0°C, and the heated again. Polarization microscopy was performed with a Zeiss Jenapol microscope, equipped with a Mettler FP 82 hot stage and a Pentacon 35 mm camera.

3.4. Blending

All the oligomers **1a–c** and **2a–c** were solution blended with PA 11 where the amount of LC oligomer in the blends 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). Oligomer **3** was not completely soluble in NMP and therefore a solution of PA 11 was as efficiently as possible stirred with oligomer **3**. After the polyamide and LC oligomers were completely dissolved they were quantitatively precipitated from excess of methanol. The blends were filtered, extracted 24 h with methanol, and then dried in a vacuum at 100°C for several hours.

3.5. Characterization of blends

DSC measurements of blends 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. Infrared spectra were measured on a Bruker IFS 66 spectrometer from KBr pellets. 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 × 2 × 2 mm³ and the test speed was 5.0 mm/min. The length of the span was 16 mm. The conventional deflection was twice the thickness of the test bar. The stress at break, σ_b , is the stress if the bar was broken before a deflection of twice the thickness of the test bar. σ_y (yield stress) is the stress at a deflection equal to twice the thickness of the test bar.

4. Conclusion

LC oligomers have been synthesized from terephthaloyl chloride and thioalkoxy (**1a–c**) and alkoxy (**2a–c**) substituted HQs. The oligomers were blended with PA 11 and the miscibility behavior of the blended compounds were measured by using DSC and FTIR analysis. The results revealed that miscibility of oligomers with PA 11 is poor.

The flexural properties of PA 11 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. A

low molecular weight LC compound with poor aggregation decreases the strength of the resulting PA 11 blend.

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References

- [1] La Mantia FP. Thermotropic liquid crystal polymer blends. Pennsylvania: Technomic Publishing, 1993.
- [2] Bonner JG, Hope PS. In: Folkes MJ, Hope PS, editors. Polymer blends and alloys, London: Blackie Academic, 1993.
- [3] Moilanen AM, Hormi OEO, Taskinen KA. *Macromolecules* 1998;31:8595.
- [4] Moilanen AM, Hormi OEO. submitted for publication.
- [5] Kolodyazhnyi YuV, Vasnev VA, Lapin EA, Alieva SA, Keshelava MG, Goguadze TsA, Vinogradova SV, Korshak VV. *Izv Akad Nauk SSSR, Ser Khim* 1975;4:778.
- [6] Biggins R, Cairns T, Eglinton G, Haslam E, Haworth RD. *J Chem Soc* 1963:1750.
- [7] Arpin M, Strazielle C. *Polymer* 1977;18:591.
- [8] Paci M, Barone C, Magagnini PL. *J Polym Sci Part B: Polym Phys* 1987;25:1595.
- [9] Paci M, Liu M, Magagnini PL, La Mantia FP, Valenza A. *Thermochim Acta* 1988;137:105.
- [10] Sargent M, Koenig JL. In: Urban MW, Craver CD, editors. *Structure–property relations in polymers*, Washington, DC: ACS, 1993. p. 191.
- [11] Hormi OEO, Moilanen AM. *Pat Appl*, PCT/FI96/00047.
- [12] Hormi OEO, Moilanen AM. *Tetrahedron* 1998;54:1943.
- [13] Kricheldorf HR, Domschke A. *Macromolecules* 1996;29:1337.