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Disubstituted 3,5-isoxazolines. An easy route to polymer liquid crystal materials

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The synthesis and phase behaviour are described of new side-chain liquid crystal polyacrylates (**9a–9d**) with a 3,5-isoxazoline ring in their mesogenic core. The new homopolymers were synthesised by free radical polymerisation. Phase transition temperatures exhibited dependence on degree of polymerisation and on terminal groups. The resulting materials exhibited typical smectic A mesomorphism.

Keywords: side-chain liquid crystal polymers; [3+2] cycloaddition; disubstituted 3,5-isoxazolines

1. Introduction

Liquid crystals are an outstanding state of matter. The liquid crystalline state is formed by a wide range of highly anisometric molecules, which gives rise to unusual, fascinating and potentially technological applications for our ''high tech'' society (*1*). There are many interesting molecular materials with geometric anisotropy, including small molecules (*2*), polymers (*3*) and materials of biological importance, such as DNA (*4*), membranes (*5*) and others (*6*), which display liquid crystalline behaviour.

In this context, side-chain liquid crystal polymers (SCLCP) have attracted attention due to their highly ordered structure. As a result, these compounds are promising substitutes for hard materials, such as ceramics, composites and other plastics. The potential applications of SCLCPs arise from the above-mentioned highly ordered structure in both glassy and molten states in addition to their chemical resistance, low flammability and high modulus (*7*).

In connection with our current interest in the synthesis of new liquid crystal polymers, we have recently prepared polyacrylate liquid crystals materials based on 3,5-isoxazoline (*8*). A phenyl moiety at the 3- and 5-positions of the isoxazoline ring assures an anisotropic shape during the polymerisation process. As part of our continuing efforts to develop liquid crystal monomers for polymerisation processes, we have prepared a new series of 3,5-disubstituted benzoyldiphenylisoxazolines (**9a–9d**), as depicted in Figure 1. This new series of polyacrylates retain their liquid crystalline properties over a large temperature range of the mesophase in the polymer state. The isoxazoline derivatives employed in the present study contain an extra benzene ring connected to the central core in order to stretch the primitive mesogenic core. The choice of a benzoyl group was due to its relative rigidity, widely used in field of liquid crystals, which contributes to the stability of the liquid crystal mesophase (*3a*), (*9*).

2. Chemistry

In order to synthesise the polyacrylates **9a–9d**, the isoxazolines derivatives **5a–5d** (see Scheme 2) were prepared as key intermediates in the synthetic approach reported here. Initially, the oxime **3** was prepared bearing a hydroxyl group suitable for further transformations. The synthesis began with protection of **1** followed by nucleophylic addition of hydroxylamine hydrochloride to the formyl group (57% in two steps, Scheme 1). During work up of the reaction in the second step, we observed spontaneous deprotection. However, this protection step was necessary due to the difficulty in removal the oxime from the aqueous layer.

The key intermediates (**5a–5d**) were synthesised, as depicted in Scheme 2. Using the [3+2] 1,3-dipolar cycloaddition reaction, were prepared four key phenols containing polar groups at the *para* position of the benzene ring. The 1,3-dipolar component nitrile oxide was obtained in situ by reacting oxime **3** with NCS in pyridine. The addition of different acceptors (**4a–4d**) to the nitrile oxide solution furnished the corresponding cycloadducts (**5a–5d**). The preparation of these isoxazolines derivatives (**5a–5d**) provided us with an entry point to a new class of precursors for high-performance liquid crystal materials.

The olefin **4a** was synthesised in this work by Wittig olefination between **6** and methyltriphenylphosphonium bromide, with 70% yield (*10*)

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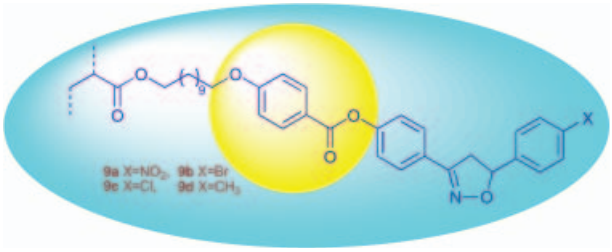
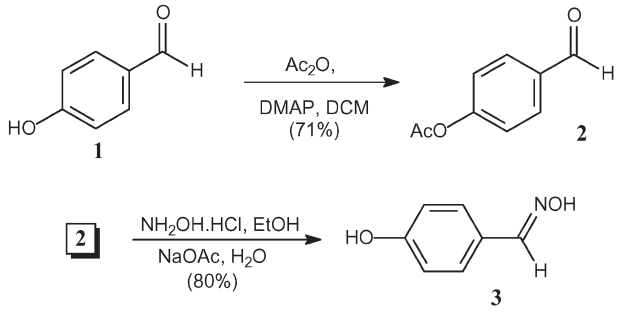


Figure 1. General chemical structures for compounds **9a–9d**.

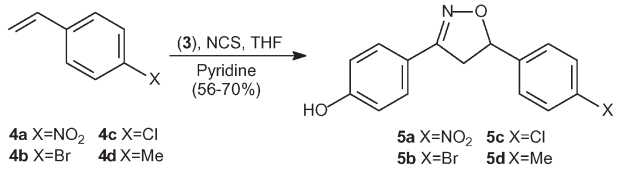
(Scheme 3). All other acceptors (**4b–4d**) are commercially available.

NMR analysis of all the intermediates (**5a–5d**) confirmed the correct regiochemistry of the cycloaddition reaction. The ^{1}H NMR spectrum for isoxazoline **5c** is shown in Figure 2. The set of three doublets between 3.00 ppm and 6.0 ppm belong to the splitting pattern of H-4 and H-5 of the 3,5-disubstituted isoxazoline ring, respectively. The resonance lines of the doublet of doublets are centred at 3.3 ppm, 3.8 ppm and 5.7 ppm. These signals, which exhibit an AMX pattern, are related to chemically and magnetically non-equivalent protons, H_A, H_M and H_X. The chemical shifts observed for the hydrogens of the heterocyclic ring provide support to confirm that only a 3,5-disubstituted regioisomer is formed. With a 3,4-disubstituted regioisomer, the chemical shifts for diastereotopic methylene and methyne hydrogens are at 5.10 ppm and 4.50 ppm, respectively (*11*). The first doubled doublet signal at 3.3 ppm in Figure 2 was assigned to the proton H_A with coupling constants $^{2}J_{gem}$ (J_{AM}) and $^{3}J_{trans}$ (J_{AX}) of 16.8 Hz and 8.5 Hz, respectively. The second doubled doublet signal at 3.8 ppm was assigned to the proton H_M and has identical coupling constant $^{2}J_{gem}$ of H_A (16.8 Hz) and coupling constant $^{3}J_{cis}$ (J_{MX}) equal to 10.9 Hz. The third resonance line centred at 5.7 ppm was assigned to the proton H_X with coupling constants $^{3}J_{cis}$ and $^{3}J_{trans}$ of 10.9 Hz and 8.5 Hz, respectively.

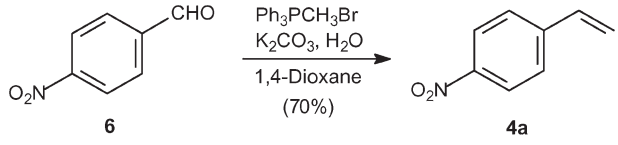
The chemical shifts and coupling constants of these signals are in accordance with 3,5-diphenylisoxazoline data from the literature (*11*). The stereochemical non-equivalence concept can be extracted from these data looking at the diastereotopic methylene hydrogens on the isoxazoline ring. The splitting patterns for the pro-*R* and pro-*S* hydrogens consist of two doubled doublets, and the relative chemical shifts are quite different. The resonance line at high field (3.3 ppm) is assigned for the pro-*R* and at low field (3.8 ppm) for the pro-*S* hydrogen (*12*). The resonance lines in the 6.5–8.0 ppm range are related



Scheme 1. Preparation of compound **3**.



Scheme 2. Synthesis of compounds **5a–5d**.



Scheme 3. Synthesis of compound **4a**.

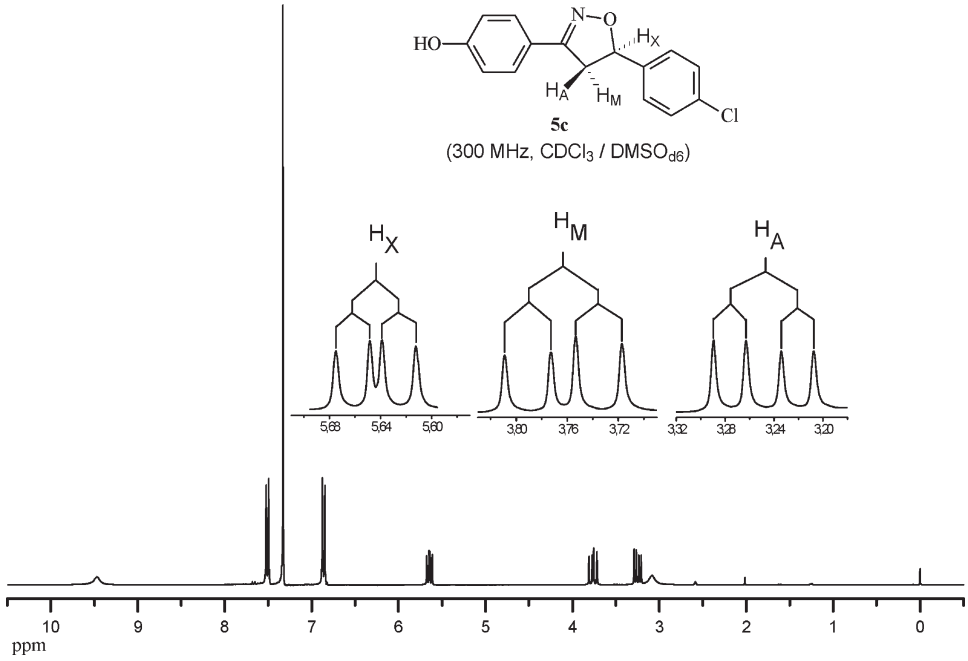
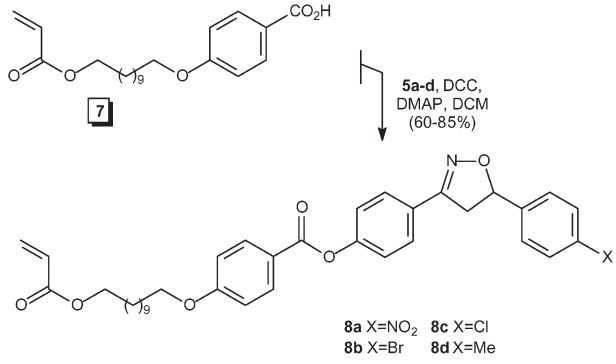


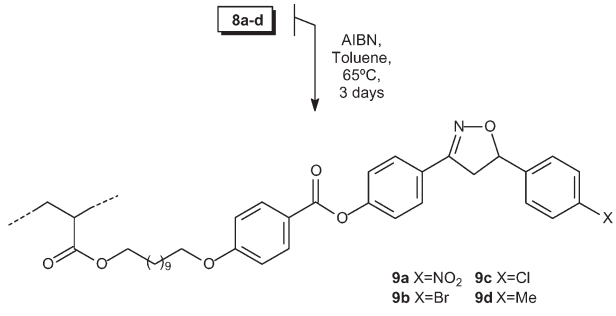
Figure 2. ^{1}H NMR spectrum ($CDCl_3$/$DMSO_{d6}$, 300 MHz) of the isoxazoline **5c**.

to aromatic hydrogens. However, accidentally, four of the eight hydrogens nuclei attached to the benzene ring have the same magnetic and chemical equivalence, resulting in the signal at 7.3 ppm.

The synthesis of monomers **8a–8d** was accomplished, as outlined in Scheme 4. The carboxylate connectivity was introduced by an esterification reaction between the isoxazolines (**5a–5d**) and the



Scheme 4. Preparation of the monomers **8a–8d**.



Scheme 5. Polymerisation conditions of monomers **8a–8d**.

Table 1. Transitions temperatures (°C) and enthalpies ($J\,g^{-1}$, in square brackets) of the monomers **8a–8d**.

Monomer	Heating/Cooling
8a	Cr_1 112.5 [16.5] Cr_2 119.7 [13.3] I / I (104.5) SmA 63.0 Cr
8b	Cr 123.2 [51.3] I / I 114.7 Cr
8c	Cr 127.4 [53.8] I / I (116) SmA 99.7 Cr
8d	Cr_1 70.6 [19.5] Cr_2 99.3 [21.1] I / I (83.4) SmA 75.3 Cr

( ) Monotropic behaviour.

acrylate **7** (*13*). The monomers were isolated and purified by recrystallisation in acetonitrile with 60–85% yield. By accessing these monomers, we easily able to synthesise our polymer liquid crystals, once they contained the key polymerisable acrylate group.

The liquid crystalline polymers were obtained through free radical polymerisation. The monomers **8a–8d** were subjected to free radical polymerisation with AIBN (5 wt %) as the radical initiator in toluene solution to give the polyacrylates **9a–9d** (Scheme 5). All polymerisation processes were performed at 65°C for 72 h under N_2 atmosphere. The polymers were precipitated in cold methanol, filtered and purified by re-precipitation from $CHCl_3$ solution, until no signal of ethylene protons in NMR spectra was observed. Finally, the polymers were dissolved in chloroform once again and filtered using a Millipore system.

3. Liquid crystalline properties

Phase transition temperatures for monomers **8a–8d** as well as the homopolymers **9a–9d** are collected in Tables 1 and 2. The homopolymers were characterised by using a Waters GPC system. Molecular weights reported in Table 2 are relative to polystyrene standards. Phase structures were studied by polarising optical microscopy (POM) and differential scanning calorimetry (DSC) measurements. The texture of the mesophase (*14*) was identified by microscopy studies on cooling from the isotropic liquid state of the samples. POM observations showed that monomers **8a**, **8c** and **8d** are liquid crystals that exhibit monotropic smectic A (SmA) behaviour. The typical texture observed on cooling is focal-conic fan-shaped for these samples. The bromine derivative **8b** did not exhibit a liquid-crystalline state.

The thermal behaviour of the polyacrylates was studied and the data are compiled in Table 2. All homopolymers are enantiotropic and exhibit the same type of mesophase. This mesophase was characterised as a smectogenic mesophase with a large temperature range. The clearing temperature observed for all polyacrylate was determined using a FT 82 hot stage system. The glass transition temperature was recorded via the DSC thermograms of samples **9a–9d**.

Figure 3 shows, as a representative example, the DSC curves and the focal-conic fan-shaped texture of the SmA mesophase produced by polymer **9a**. In this case, upon cooling from the clearing point at 204°C, a SmA phase emerges as bâtonnet quickly at 201–203°C from the isotropic liquid and finally the bâtonnets coalesce to exhibit the typical focal-conic fan-shaped indicative of a layered structure to polymer **9a**. In addition, some regions of homeotropic texture are formed, leading us to conclude that the director of the phase is orthogonal to the layer planes. Consequently, the observed phase was assigned as smectic A.

The glass transition temperature in these polymers is related to the average degrees of polymerisation (DP) and to the nature of the group attached to the benzene ring. The DP for these compounds is low, especially for compound **9b**. However, the influence of DP on the existence of the mesomorphic behaviour is not so decisive. For example, the homopolymers (oligomers) **9a** (ΔT=111.3°C) and **9b** (ΔT=119°C) display similar a temperature range for the mesophase. However, **9a** is approximately twice as heavy as **9b**. Comparison between **9a** and **9c**, which have identical DP, shows that mesophase behaviour is mainly dependent on the terminal group bonded to the benzene ring. The temperature range for **9a**

Table 2. Thermal properties of the homopolymers **9a–9d** (g=glass phase; SmA=smectic A phase; I=isotropic phase; PD=polydispersity; DP=number average degrees of polymerization). Clearing temperatures were determined using an FT 82 hot stage system.

Polymer	M_n/g mol^{-1}	PD	DP	Yield /%	g	/°C	SmA	/°C	I	ΔH[a]
9a	5999	1.21	9.5	50	•	92.7	•	204	•	15.8
9b	2678	1.90	4.0	57	•	[b]	•	209	•	[c]
9c	5884	1.18	9.5	62	•	127.0	•	212	•	15.9
9d	9015	1.70	15.0	84	•	73.0	•	175	•	[c]

[a]Enthalpy values (ΔH, $J\,g^{-1}$) were determined for the transition from the glassy phase to smectic A phase. [b]The T_g value (90°C) of **9b** was observed only on the first heating. During the 2nd and 3rd scans the peak tends to disappear. [c]Value not determined.

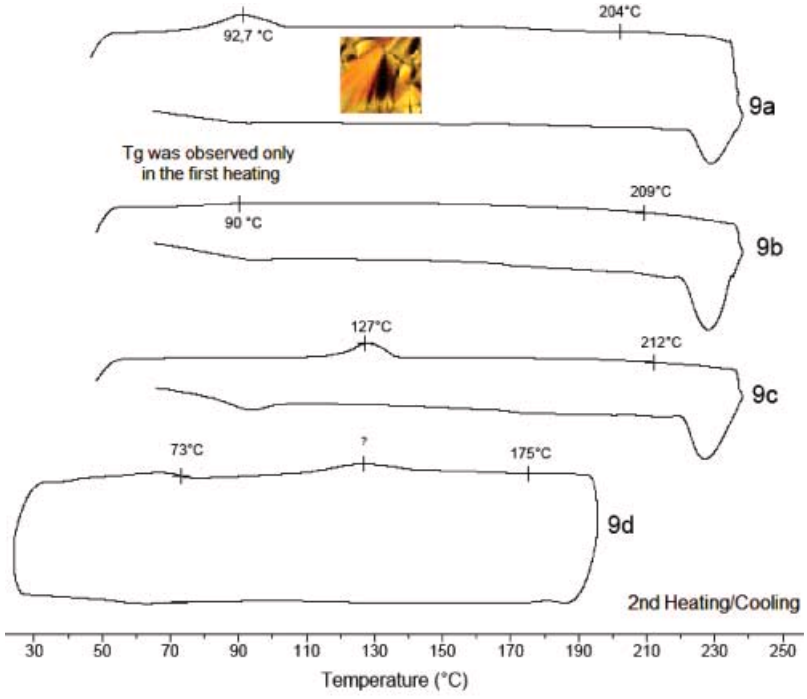


Figure 3. DSC thermograms for polyacrylates **9a–9d**. The texture of the SmA mesophase was unchanged around the depression point for **9d** near 127°C. The origin of this behaviour is uncertain.

($X=NO_2$) is higher than that for **9c** ($X=Cl$) probably due to polarisability and flatness of the nitro group. The homopolymer **9d** ($X=CH_3$) has a larger thermal range of the mesophase ($\Delta T=117°C$), and this could be related to the high degree of polymerisation. For all materials prepared in this study, the degree of polymerisation has a strong influence on the ordering of the mesogenic groups. The polymerisation action enforces the monomers to align with each other, even though the hard core of this kind of molecule is deviated from linearity and flatness due to the presence of an isoxazoline ring at the middle of the mesogenic hard core. From this study we can conclude that the efficiency of the terminal group in stabilising the smectic A liquid crystal phase follows the sequence $Br \sim NO_2 > CH_3 > Cl$. These results are in accordance with those of previous studies (*8*).

In summary, we have synthesised, in five steps, four homopolymers having an isoxazoline ring as the key structural component that results in mesomorphic phenomena. The polymers exhibit smectic A enantiotropic behaviour over a large temperature range. The liquid crystal properties are dependent on the degree of polymerisation and on the terminal group. These are important parameters to be considered in the design and synthesis of new materials. To overcome the structural constraints due to the isoxazoline system, further studies concerning preparation of the corresponding isoxazol systems are in progress.

4. Experimental

^1H NMR and ^{13}C NMR spectra in $CDCl_3$ were obtained using Varian-200 and 300 MHz spectrometers using TMS as an internal standard. IR spectra were recorded in Nujol on a 3000 Galaxy Series spectrometer. The thermal transitions and the textures were determined using an Olympus BX43 polarising microscope in conjunction with a Mettler FP90 controller and HT84 heating stage and Perkin Elmer 141 differential scanning calorimeter. The rate of heating or cooling was $10°C\,min^{-1}$.

The reagents methyltriphenylphosphonium bromide, hydroxylamine chloridrate, 4-hydroxybenzaldehyde, pyridine, 11-bromoundecan-1-ol, acrylic acid, *N*-chlorosuccinimide (NCS), *p*-bromostyrene, *p*-chlorostyrene, *p*-toluenesulfonic acid (pTSA), *p*-methylstyrene and hydroquinone were used as received from Aldrich Co. Analytical thin layer chromatography (TLC) was conducted on Merck aluminium plates with 0.2 mm of sílica gel 60F-254. Anhydrous sodium sulfate was used to dry all organic extracts. Toluene and THF were first heated at reflux over sodium and then distilled under argon. AIBN was freshly recrystallised from methanol. Purification by column chromatography was carried out on 70-230 mesh Merck sílica gel 60. All other solvents and reagents were used without previous purification.

Syntheses

*4-Formylphenyl acetate (**2**).*

A mixture of *p*-hydroxybenzaldehyde (0.49 g, 4 mmol), acetic anhydride (0.57 ml, 6 mmol), DMAP (0.01 g, 0.8 mmol) and dichloromethane (10ml) was stirred at room temperature for 2 h. The solvent was distilled, ethyl ether (20 ml) was added and the organic solution was washed with sodium bicarbonate 5% (2 × 50 ml), water (2 × 50 ml) and dried over anhydrous sodium sulfate. The solvent was removed in vacuum, resulting in a yellow liquid, in 71% yield, which was used without purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.3 (s, 3H, CH_3CO), 7.3 (d, 2H, Ar, J=8.6 Hz), 7.9 (d, 2H, Ar, J=8.6 Hz), 9,9 (s, 1H, COH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.1, 122.2, 131.0, 133.7, 155.1, 168.6, 190.9. IR (nujol, cm^{-1}): 2833, 1751, 1701, 1591, 1196, 1010, 833.

*4-Hydroxybenzaldehyde oxime (**3**).*

To an aqueous solution of 4-formylphenyl acetate (0.44 g, 2.7 mmol) was added hydroxylamine chloridrate (0.53 g, 7.6 mmol) in ethanol (5 ml) and sodium acetate (0.89 g, 10.8 mmol). The mixture was refluxed for 40 min and the water removed under vacuum. To the solid residue was added ethyl ether (15 ml) and the ethereal layer was dried over anhydrous sodium sulfate. The solvent was removed furnishing the oxime **3** as pale yellow solid. Yield: 80%. M.p. 77–79°C. ^{1}H NMR (D_2O, 300 MHz): 6.9 (d, 2H, Ar, J=8.7 Hz), 7.4 (d, 2H, Ar, J=8.7 Hz), 8.0 (s, 1H, CHNOH). ^{13}C NMR (D_2O, 75 MHz): δ 115.8, 123.7, 129.0, 151.6, 157.7. IR (nujol, cm^{-1}): 3520–2625, 1693, 1606, 1512, 1427, 1199, 829.

*1-Nitro-4-vinylbenzene (**4a**).*

4-Nitrobenzaldehyde (1.03 g, 6.8 mmol), methyltriphenylphophonium bromide (7.3 g, 20,4 mmol) and sodium carbonate (2.8 g, 20.4 mmol) were dissolved in dioxane (80 ml) and water (8 ml) and the mixture heated under reflux for three days. The aqueous phase was extracted with ethyl ether (100 ml), and the ethereal layer was washed with water (3 × 50 ml) and dried over anhydrous sodium sulfate. After filtration the solvent was removed to give a yellow liquid. Chromatography on silica gel with ethyl acetate:hexane (1:49) as eluent afforded compound **4a** (70% yield). M.p. 20°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.5 (d, 1H, CH=CH_2, $^3J_{cis}$=10.8 Hz), 5.9 (d, 1H, CH=CH_2, $^3J_{trans}$=17.7 Hz), 6.8 (dd, 1H, CH=CH_2, $^3J_{cis}$=10.8 Hz, $^3J_{trans}$=1 7.7 Hz), 7.5 (d, 2H, Ar, J=8.8 Hz), 8.2 (d, 2H, Ar, J=8.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 118.5, 123.8, 126.7, 134.8, 143.7, 147.0. IR (nujol, cm^{-1}): 3448, 2930, 1701, 1600, 1527, 1090, 854.

*4-[5-(4-nitrophenyl)-4,5-dihydroisoxazol-3-yl]phenol (**5a**).*

The representative procedure is described for compound **5a**. To a solution of 4-nitrostyrene (0.42 g, 2.8 mmol), *N*-chlorosuccinimide (0.56 g, 4.2 mmol) and pyridine (0.34 ml, 4.2 mmol) in tetrahydrofuran (12 ml) at 0°C under an argon atmosphere was added dropwise a solution of 4-hydroxybenzaldehyde oxime (0.38 g, 2.8 mmol) in tetrahydrofuran. The mixture was stirred at room temperature for 4 h. The solvent was evaporated in vacuum and the residue was dissolved in ethyl ether (30 ml). The solution was washed with HCl 1M (3 × 20 ml), $NaHCO_3$ 5% (20 ml) and water (20 ml) and then dried over Na_2SO_4. After filtration the solvent was removed and the product was recrystallised in CH_3CN. Yield: 56%. M.p. 146–147°C. ^{1}H NMR ($CDCl_3$/$DMSO_{d6}$, 300 MHz): δ 3.3 (dd, 1H, C<u>H</u>HCH, $^3J_{trans}$=.5 Hz, $^2J_{gem}$=16.8 Hz), 3.9 (dd, 1H, CH<u>H</u>CH, $^3J_{cis}$=10.9 Hz, $^2J_{gem}$=16.8 Hz), 5.8 (dd, 1H, CHHC<u>H</u>, $^3J_{trans}$=8.5 Hz, $^3J_{cis}$=10.9 Hz), 6.9 (d, 2H, Ar, J=8.7 Hz), 7.5 (s, 2H, Ar, J=8.7 Hz), 7.6 (d, 2H, Ar, J=8.7 Hz), 8.2 (d, 2H, Ar, J=8.7 Hz), 8.4 (s, 1H, OH, broad). ^{13}C NMR ($CDCl_3$/$DMSO_{D6}$, 75 MHz): δ 43.8, 80.8, 116.1, 120.0, 124.1, 127.1, 128.7, 147.7, 149.1, 156.1, 159.9. IR (nujol, cm^{-1}): 3400, 2256, 1654, 1514, 1348, 997.

For **5b**, yield: 70%. M.p. 172–175°C. ^{1}H NMR ($CDCl_3$/$DMSO_{d6}$, 300 MHz): δ 3.3 (dd, 1H, C<u>H</u>HCH, $^3J_{trans}$=8.5 Hz, $^2J_{gem}$=16.8 Hz), 3.8 (dd, 1H, CH<u>H</u>CH, $^3J_{cis}$=10.9 Hz, $^2J_{gem}$=16.8 Hz), 5.6 (dd, 1H, CHHC<u>H</u>, $^3J_{trans}$=8.5 Hz, $^3J_{cis}$=10.9 Hz), 6.9 (d, 2H, Ar, J=8.7 Hz), 7.3 (s, 2H, Ar, J=8.7 Hz), 7.5 (d, 4H, Ar, J=8.7 Hz), 9.2 (s, 1H, OH, broad). ^{13}C NMR ($CDCl_3$/$DMSO_{D6}$, 75 MHz): δ 43.2, 81.4, 115.8, 120.2, 126.4, 127.0, 128.3, 131.7, 140.1, 155.9, 159.1. IR (nujol, cm^{-1}): 3344, 3000, 1602, 1516, 1355, 1277, 1225, 816.

For **5c**, yield: 58%. M.p. 178–180°C. ^{1}H NMR ($CDCl_3$/$DMSO_{d6}$, 300 MHz): δ 3.3 (dd, 1H, C<u>H</u>HCH, $^3J_{trans}$=8.5 Hz, $^2J_{gem}$=16.8 Hz), 3.8 (dd, 1H, CH<u>H</u>CH, $^3J_{cis}$=10.9 Hz, $^2J_{gem}$=16.8 Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{trans}$=8.5 Hz, $^3J_{cis}$=10.9 Hz), 6.9 (d, 2H, Ar, J=8.7 Hz), 7.3 (s, 4H, Ar, J=8.7 Hz), 7.5 (d, 2H, Ar, J=8.7 Hz), 9.4 (s, 1H, OH, broad). ^{13}C NMR ($CDCl_3$/$DMSO_{D6}$, 75 MHz): δ 43.2, 81.0, 115.6, 120.4, 127.0, 128.1, 128.5, 133.5, 139.5, 155.8, 159.1. IR (nujol, cm^{-1}): 3143, 1596, 1272, 1174, 829.

For **5d**, yield: 63%. M.p. 174°C. ^{1}H NMR ($CDCl_3$/$DMSO_{d6}$, 300 MHz): δ 2.4 (s, 3H, CH_3), 3.4 (dd, 1H, C<u>H</u>HCH, $^3J_{trans}$=8.5 Hz, $^2J_{gem}$=16.8 Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^3J_{cis}$=10.9 Hz, $^2J_{gem}$=16.8 Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{trans}$=8.5 Hz, $^3J_{cis}$=10.9 Hz), 6.9 (d, 2H, Ar, J=8.7 Hz), 7.2 (d, 2H, Ar, J=8.7 Hz), 7.3 (d, 2H, Ar, J=8.7 Hz), 7.5 (d, 2H, Ar, J=8.7 Hz), 9.5 (s, 1H, OH, broad). ^{13}C NMR ($CDCl_3$/$DMSO_{d6}$,

75 MHz): δ 20.8, 43.1, 81.7, 115.5, 120.2, 125.6, 128.0, 129.0, 137.5, 137.7, 155.7, 158.9. IR (nujol, cm^{-1}): 3410, 3097, 1591, 1514, 1437, 1278, 1169, 843, 800.

*4-[11-(acryloyloxy)undecyloxy]benzoic acid (**7**).*

This compound was synthesised according to a literature method (*11*). Yield: 58%, white solid. M.p. 94°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.4 (m, 14H, $(CH_2)_7$), 1.7 (m, 4H, CH_2), 4.0 (t, 2H, CH_2O), 4.1 (t, 2H, CH_2O,), 5.8 (dd, 1H, J_{cis}=10.3 Hz, J_{gem}=1.5 Hz, CH=CH_2), 6.1 (dd, J_{trans}=17.3 Hz, J_{cis}=10.3 Hz, 1H, CH=CH_2), 6.4 (dd, J_{trans}=17.3 Hz, J_{gem}=1.5 Hz, 1H, CH=CH_2), 6.9 (d, 2H, Ar, J=8.9 Hz), 8.0 (d, 2H, Ar, J=8.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.8, 25.9, 28.5, 29.0, 29.2, 29.4, 32.5, 64.7, 68.1, 114.1, 121.4, 128.5, 130.4, 132.2, 163.6, 166.4, 171.8. IR (nujol, cm^{-1}): 2925, 1726, 1679, 1602, 1427, 1255, 1167, 850.

*4-[5-(4-nitrophenyl)-4,5-dihydroisoxazol-3-yl]phenyl 4-[11-(acryloyloxy)undecyl-oxy]benzoate (**8a**).*

The representative procedure is described for compound **8a**. Compound **5a** (0.80 g, 2.8 mmol) and acid **7** (1.01 g, 2.8 mmol) were dissolved in dry tetrahydrofuran (20 ml) under argon and the organic solution stirred at room temperature for 10 min. After this, DCC (7.5 g, 3.64 mmol) and DMAP (0.03 g, 0.28 mmol) were added, and the mixture was stirred for 48 h at room temperature. The resulting solution was filtered and the solvent was evaporated. The crude product was purified by recrystallisation from ethanol. Yield: 70%, pale yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.4 (m, 12H, $(CH_2)_6$), 1.6 (m, 2H, C$\underline{H_2}$CH_2O), 1.8 (m, 2H, C$\underline{H_2}$CH_2OCO), 3.3 (dd, 1H, C$\underline{H}$HCH, $^3J_{trans}$=8.5 Hz, $^2J_{gem}$=16.8 Hz), 3.9 (dd, 1H, CH$\underline{H}$CH, $^3J_{cis}$=10.9 Hz, $^2J_{gem}$=16.8 Hz), 4.0 (t, 2H, CH_2O), 4.2 (t, 2H, CH_2O,), 5.8 (dd, 1H, CHHC$\underline{H}$, $^3J_{trans}$=8.5 Hz, $^3J_{cis}$=10.9 Hz), 5.9 (dd, 1H, CH=CH_2, $^2J_{gem}$=1.6 Hz, $^3J_{cis}$=10.6 Hz), 6.1 (dd, 1H, CH=CH_2, $^3J_{cis}$=10.6 Hz, $^3J_{trans}$=17.2 Hz), 6.4 (dd, 1H, CH=CH_2, $^2J_{gem}$=1.6 Hz, $^3J_{trans}$=17.2 Hz), 7.0 (d, 2H, Ar, J=8.8 Hz), 7.3 (d, 2H, Ar, J=8.8 Hz), 7.6 (d, 2H, Ar, J=8.8 Hz), 7.7 (d, 2H, Ar, J=8.8 Hz), 8.1 (d, 2H, Ar, J=8.8 Hz), 8.2 (d, 2H, Ar, J=8.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.9, 28.6, 29.0, 29.1, 29.4, 43.4, 64.7, 68.3, 81.2, 114.3, 121.0, 122.4, 124.0, 126.3, 128.1, 128.6, 129.7, 129.9, 130.7, 132.3, 148.1, 152.7, 155.3, 163.7, 164.5, 166.3. IR (nujol, cm^{-1}): 2920, 1724, 1602, 1517, 1352, 1263, 1205, 840.

For **8b**, yield 62%, pale yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.4 (m, 12H, $(CH_2)_6$), 1.7 (m, 2H, C$\underline{H_2}$CH_2O), 1.8 (m, 2H, C$\underline{H_2}$CH_2OCO), 3.3 (dd, 1H, C$\underline{H}$HCH, $^3J_{trans}$=8.5 Hz, $^2J_{gem}$=16.8 Hz), 3.8 (dd, 1H, CH$\underline{H}$CH, $^3J_{cis}$=10.9 Hz, $^2J_{gem}$=16.8 Hz), 4.0 (t, 2H, CH_2O), 4.2 (t, 2H, CH_2O,), 5.7 (dd, 1H, CHHC$\underline{H}$, $^3J_{trans}$=8.5 Hz, $^3J_{cis}$=10.9 Hz), 5.8 (dd, 1H, CH=CH_2, $^2J_{gem}$=1.6 Hz, $^3J_{cis}$=10.6 Hz), 6.1 (dd, 1H, CH=CH_2, $^3J_{cis}$=10.6 Hz, $^3J_{trans}$=17.2 Hz), 6.4 (dd, 1H, CH=CH_2, $^2J_{gem}$=1.6 Hz, $^3J_{cis}$=17.2 Hz), 7.0 (d, 2H, Ar, J=8.8 Hz), 7.2 (d, 2H, Ar, J=8.8 Hz), 7.3 (d, 2H, Ar, J=8.8 Hz), 7.5 (d, 2H, Ar, J=8.8 Hz), 7.7 (d, 2H, Ar, J=8.8 Hz), 8.1 (d, 2H, Ar, J=8.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.1, 28.2, 28.3, 28.4, 28.5, 42.1, 63.6, 67.3, 80.9, 113.5, 121.4, 122.5, 125.8, 126.8, 127.0, 127.6, 129.5, 129.8, 130.8, 131.3, 139.1, 151.5, 154.5, 160.8, 162.7, 163.6. IR (nujol, cm^{-1}): 2916, 1728, 1606, 1508, 1284, 1208, 1070, 840.

For **8c**, yield 60%, pale yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.4 (m, 12H, $(CH_2)_6$), 1.7 (m, 2H, C$\underline{H_2}$CH_2O), 1.8 (m, 2H, C$\underline{H_2}$CH_2OCO), 3.3 (dd, 1H, C$\underline{H}$HCH, $^3J_{trans}$=8.5 Hz, $^2J_{gem}$=16.8 Hz), 3.8 (dd, 1H, CH$\underline{H}$CH, $^3J_{cis}$=10.9 Hz, $^2J_{gem}$=16.8 Hz), 4.0 (t, 2H, CH_2O), 4.1 (t, 2H, CH_2O,), 5.7 (dd, 1H, CHHC$\underline{H}$, $^3J_{trans}$=8.5 Hz, $^3J_{cis}$=10.9 Hz), 5.8 (dd, 1H, CH=CH_2, $^2J_{gem}$=1.6 Hz, $^3J_{cis}$=10.6 Hz), 6.1 (dd, 1H, CH=CH_2, $^3J_{cis}$=10.6 Hz, $^3J_{trans}$=17.2 Hz), 6.4 (dd, 1H, CH=CH_2, $^2J_{gem}$=1.6 Hz, $^3J_{trans}$=17.2 Hz), 7.0 (d, 2H, Ar, J=8.8 Hz), 7.3 (d, 2H, Ar, J=8.8 Hz), 7.4 (m, 4H, Ar, J=8.8 Hz), 7.7 (d, 2H, Ar, J=8.8 Hz), 8.1 (d, 2H, Ar, J=8.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.2, 28.8, 29.3, 29.5, 29.7, 43.5, 65.0, 68.6, 82.1, 114.6, 121.3, 122.6, 125.5, 127.0, 127.8, 128.2, 128.6, 129.2, 130.7, 132.5, 139.6, 152.8, 155.6, 160.8, 164.0, 164.8. IR (nujol, cm^{-1}): 2918, 1728, 1606, 1508, 1259, 1168, 1072, 823.

For **8d**, yield 85%, pale yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9 (t, 3H, CH_3); 1.6 (m, 14H, $(CH_2)_7$), 2.4 (m, 4H, C$\underline{H_2}$CH_2O), 3.3 (dd, 1H, C$\underline{H}$HCH, $^3J_{cis}$=8.4 Hz, $^2J_{gem}$=16.8 Hz), 3.8 (dd, 1H, CH$\underline{H}$CH, $^3J_{cis}$=11.1 Hz, $^2J_{gem}$=16.8 Hz), 4.1 (t, 2H, CH_2O), 4.2 (t, 2H, CH_2O), 5.7 (dd, 1H, CHHC$\underline{H}$, $^3J_{trans}$=8.4 Hz, $^3J_{cis}$=10.8 Hz), 5.8 (dd, 1H, CH=CH_2, $^2J_{gem}$=1.8 Hz, $^3J_{cis}$=10.8 Hz), 6.1 (dd, 1H, CH=CH_2, $^3J_{cis}$=10.2 Hz, $^3J_{trans}$=17.1 Hz), 6.4 (dd, 1H, CH=CH_2, $^2J_{gem}$=1.5 Hz, $^3J_{trans}$=17.4 Hz), 7.0 (d, 2H, Ar, J=9.0 Hz), 7.2 (d, 2H, Ar, J=8.7 Hz), 7.28 (d, 2H, Ar, J=8,7 Hz), 7.31 (d, 2H, Ar, J=8.7 Hz), 7.8 (d, 2H, Ar, J=9.0 Hz), 8.2 (d, 2H, Ar, J=9.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.4, 26.1, 26.2, 29.7, 29.8, 34.1, 43.3, 60.2, 64.9, 68.5, 82.9, 114.6, 122.5, 123.4, 125.7, 126.1, 128.1, 129.2, 129.6, 131.8, 132.5, 138.0, 138.3, 152.6, 155.7, 163.9, 164.8, 166.5. IR (nujol, cm^{-1}): 3440, 2920, 2844, 2364, 1728, 1606, 1558, 1412, 1209, 810.

Polymerisation.

All polymerisations processes were performed at 65°C for 72 h under N_2 atmosphere using as initiator

2,2′-azobisisobutyronitrile AIBN (5 wt %). The polymers were precipitated in cold methanol, filtered and purified by re-precipitation from $CHCl_3$ solutions until no signal of ethylene protons in ^1H NMR spectra could be observed. Subsequently, the polymers were dissolved in chloroform once again and filtered using a Millipore system and dried in vacuum. Molecular weights reported in Table 2 are relative to polystyrene standards and they have been characterised using a Waters GPC system (Waters 150C refractometer).

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