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Molecular engineering of liquid crystal polymers by living polymerization

4. Synthesis and cationic polymerization of some mesogenic vinyl ethers containing various functional groups

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SUMMARY

The synthesis of 11-[(4'-methoxy-4-biphenyl)oxy]undecanyl vinyl ether (4), 11-[(4'-nitro-4-biphenyl)oxy]undecanyl vinyl ether (13), 11-[p(4-cyanophenylbenzoate)oxy]undecanyl vinyl ether (17) and 3-[2-[1,2,2-trifluoroethoxy]-2-(4-methoxy-4-(α-methylstilbene)oxy]-1-(trifluoromethyl)trifluoroethoxy)-1-[2-(ethyloxy)ethoxy]-2,2,3,3-tetrafluoropropane (22) and their cationic polymerization with the initiating system $H_2O/AlEtCl_2/(CH_3)_2S$ is described. All the functional groups available in these monomers, i.e., nucleophilic aromatic groups, nitro and cyano groups, aromatic esters, double bonds and acidic protons are tolerated by this polymerization technique. The resulting polymers exhibit narrow molecular weight distribution and display mesomorphic behavior. With the exception of poly(4) which exhibits a monotropic s_A mesophase, all other polymers display an enantiotropic s_A mesophase.

INTRODUCTION

Previous publications from our laboratory surveyed various living polymerization techniques which have the potential of being used in the molecular engineering of liquid crystalline polymers.[1-5] Of them, group transfer polymerization of mesogenic methacrylates[2] and cationic polymerization of mesogenic vinyl ethers[3-7] were the most succesful. In particular living cationic polymerization initiated by a system based on a source of proton, a nonnucleophilic counterion and a Lewis base like for example $(CH_3)_2S$[8,9] can be performed in polar solvents like methylene chloride and at temperatures as high as 0°C. Other cationic initiating systems which require a lower polymerization temperature and a nonpolar solvent can be used as well.[10-12]

The goal of this paper is to investigate the range of functional groups present in the monomeric structure which are tolerated by the cationic polymerization technique. With this goal in mind this paper will describe the synthesis and polymerization of a monomer which contains a very nucleophilic mesogenic group, i.e., 11-[(4'-methoxy-4-biphenyl)oxy]undecanyl vinyl ether (4), a monomer which has a nitro group, i.e., 11-[(4'-nitro-4-biphenyl)oxy]undecanyl vinyl ether (13), a monomer which contains both a cyano and an aromatic ester group, i.e., 11-[(4-cyanophenylbenzoate)oxy]undecanyl vinyl ether (17), and a semiflorinated monomer which contains both a double bond and a very acidic proton, i.e., 3-[2-[1,2,2-trifluoroethoxy-2-(4-methoxy-4-(α-methylstilbene)oxy]-1-(trifluoromethyl)-trifluoroethoxy)-1-[2-(ethyloxy)ethoxy]-2,2,3,3-tetrafluoropropane (22). The mesomorphic characterization of the resulting polymers will be also described.

EXPERIMENTAL

Schemes I-IV outline the synthesis of all monomers.

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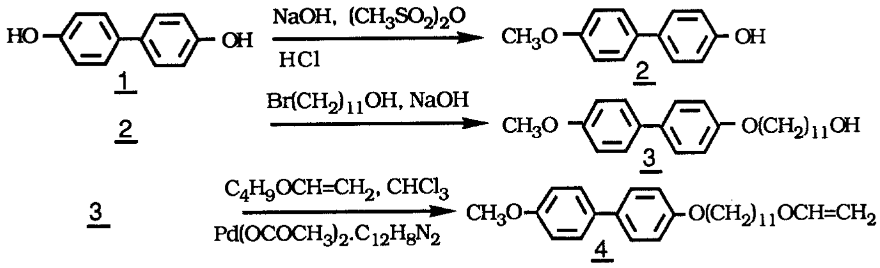
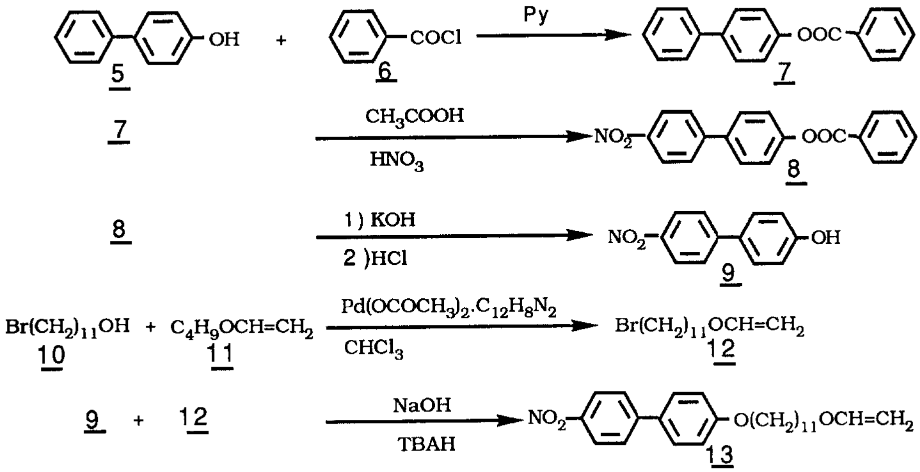
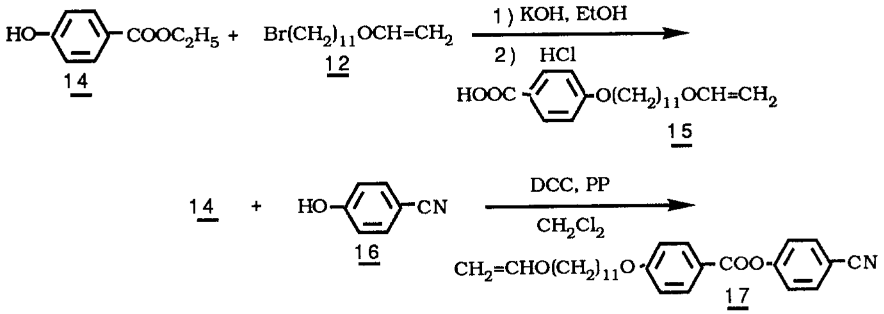


Scheme I: Synthesis of 4



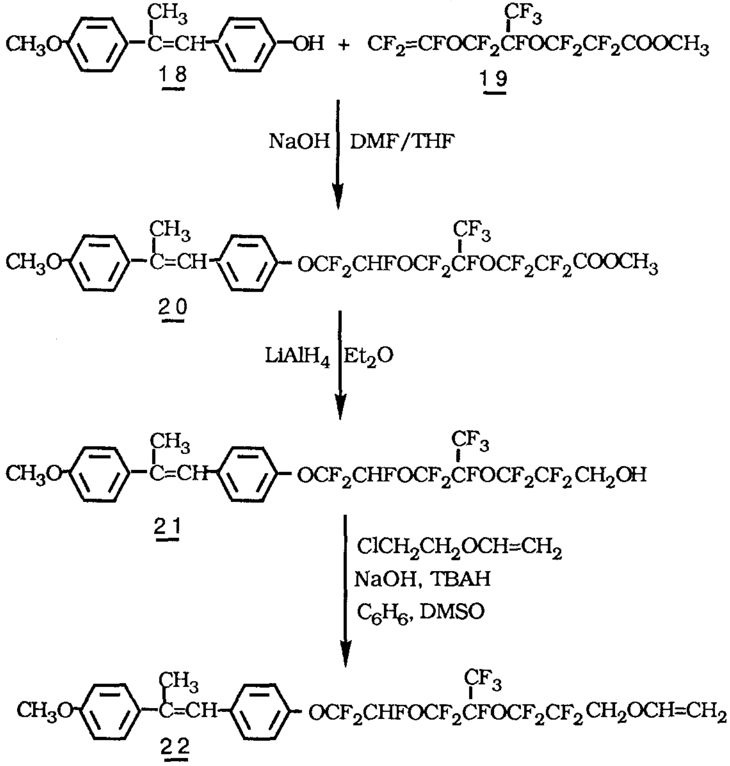
Scheme II: Synthesis of 13



Scheme III: Synthesis of 17

Materials

11-(4'-Methoxy-4-biphenyloxy)undecanol (3)[13], 4'-nitro-4-hydroxybiphenyl (9)[14], 4-methoxy-4'-hydroxy-α-methylstilbene (18)[15], 11-bromoundecanyl vinyl ether (11)[3], and 1,10-phenanthroline palladium(II) diacetate[3] were synthesized as described in a previous paper from our laboratory. The other reagents were used as received or were purified as described in previous publications. Me_2S, $EtAlCl_2$ and CH_2Cl_2 used in polymerization experiments were purified as previously described.[5] The last purification of monomers was performed by column chromatography (alumina, CH_2Cl_2 eluent) in order to eliminate all protonic impurities.



Scheme IV: Synthesis of 22

Synthesis of monomers

4-Methoxy-4'-(11-hydroxyundecan-1-yloxy)biphenyl (3)

3 was synthesized as reported in a previous publication.[13]

11-[(4'-Methoxy-4-biphenyl)oxy]undecanyl Vinyl Ether (4)

4-Methoxy-4'-(11-hydroxyundecan-1-yloxy)biphenyl (3) (1.80 g, 4.86 mmol) was added to a heterogeneous mixture containing 0.20 g (0.49 mmol) of 1,10-phenanthroline palladium(II) diacetate, 26 ml of n-butyl vinyl ether and 7 ml $CHCl_3$. The reaction mixture was stirred at 65 °C for 7 hr. After cooling to room temperature, the reaction mixture was filtered to remove the catalyst and the solvent was removed in a rotavapor. Purification by column chromatography using silica gel and CH_2Cl_2 as eluent afforded 1.4 g (74%) of a white solid. Purity (HPLC) 99%. mp (DSC) 95°C. ^1H-NMR($CDCl_3$, TMS, δ, ppm): 1.30-1.82 (18 protons, $-(C\underline{H}_2)_9-$, m) 3.68 (2 protons, $-C\underline{H}_2O-$, t), 3.84 (3 protons, $-OC\underline{H}_3$, s), 3.99 (3 protons, one cis from $OCH{=}C\underline{H}_2$ and 2 from $PhOC\underline{H}_2-$, m), 4.18 (1 proton, $OCH{=}C\underline{H}_2$, trans, d), 6.47 (1 proton, $OC\underline{H}{=}CH_2$, q), 6.98 and 7.00 (4 aromatic protons, o to -O-, 2d), 7.45 and 7.56 (4 aromatic protons, m to -O-, 2d)

4'-Nitro-4-hydroxybiphenyl (9)

9 was synthesized according to a literature procedure.[14]

11-[(4'-Nitro-4-biphenyl)oxy]undecanyl Vinyl Ether (13)

A reaction mixture containing 0.64 g (2.97 mmol) of 4'-nitro-4-hydroxybiphenyl (9), 0.91 g (3.27 mmol) 11-bromoundecanyl vinyl ether (11)[3], 0.9 ml (9.00 mmol) 10N NaOH, 4 ml of a mixture of benzene/dimethylsulfoxide (1/5, v/v) and 0.15 g (0.45 mmol) tetrabutylammonium hydrogen sulfate was stirred at 70 °C for 25 hr. After cooling to room temperature, the organic phase was washed with water and the solvent was evaporated in a rotavapor. The resulting product was purified by column chromatography (silica gel, CH_2Cl_2 eluent) and recrystallized twice from ethanol to yield 0.97 g (80%) of crystals. Purity (HPLC) 99.5%. mp (DSC) 97 °C. ^1H-NMR ($CDCl_3$, TMS, δ, ppm): 1.32-1.85 (18 protons, $-(C\underline{H}_2)_9-$, m), 3.68 (2 protons, $-C\underline{H}_2O-$,t), 4.02 (3 protons, one cis from $OCH{=}C\underline{H}_2$ and two from $PhOC\underline{H}_2-$, m), 4.18 (1 proton, $OCH{=}C\underline{H}_2$ trans, d), 6.48 (1 proton, $OC\underline{H}{=}CH_2$, q), 7.02 (2 aromatic protons, o to -O-, d), 7.57 (2 aromatic protons, m to -O-, d), 7.70 (2 aromatic protons, m to $-NO_2$, d), 8.28 (2 aromatic protons, o to $-NO_2$, d).

11-[p(Benzoic acid)oxy]undecanyl Vinyl Ether (15)

A reaction mixture containing 3.00 g (10.8 mmol) 11-bromoundecanyl vinyl ether (12), 1.80 g (10.8 mmol) ethyl 4-hydroxybenzoate (14), 0.67 g (11.9 mmol) KOH and 60 ml ethanol (97.5%) was heated at reflux for 23 hr. KOH (3.01 g, 53.6 mmol) was added and the reaction was continued at reflux temperature for additional 12 hr. After cooling to room temperature the reaction mixture was neutralized with 1 mol HCl, the precipitate was filtered, washed with water and ethanol and recrystallized from ethanol to yield 2.7 g (75%) of 14. This product was used in the next step without further purification.

11-[p(4-Cyanophenylbenzoate)oxy]undecanyl Vinyl Ether (17)

To a solution of 15 (2.70 g, 8.07 mmol) and 4-cyanophenol (16) (0.96 g, 8.07 mmol) in 40 ml dry CH_2Cl_2 were added at 0 °C 1.83 g (0.88 mmol) 1,3-dicyclohexylcarbodiimide (DCC) and 1.20 g (8.07 mmol) 4-pyrrolidinopyridine. The reaction mixture was heated at reflux temperature for 3 days. The resulting precipitate (1,3-dicyclohexylurea) was filtered and the solvent was evaporated in a rotavapor. The resulting solid was purified by column chromatography (silica gel) by using a gradient of ethyl acetate/hexane and then was recrystallized twice from ethanol to yield 1.7g (49%) of white crystals. Purity (HPLC) 99.9%. mp (DSC), 72°C. ^1H-NMR ($CDCl_3$, TMS,δ, ppm): 1.22-1.57 (14 protons, $-(C\underline{H}_2)_7-$, m), 3.68 (2 protons, $-C\underline{H}_2O-$, t), 4.05 (2 protons, $PhOC\underline{H}_2-$, t), 3.98 (1 proton, $C\underline{H}_2{=}CHO-$ cis, d), 4.18 (1 proton, $C\underline{H}_2{=}CHO-$ trans, d), 6.47 (1 proton, $CH_2{=}C\underline{H}O-$, q), 6.99 (2 aromatic protons o from -O- of benzoate group, d), 8.13 (2 aromatic protons, o from ester of benzoate group, d), 7.36 (2 aromatic protons, m from -CN, d), 7.36 (2 aromatic protons, m from -CN, d).

4-Methoxy-4'-hydroxy-α-methylstilbene (18)

18 was synthesized as described previously.[15]

3-[2-(1,2,2-Trifluoroethoxy)-2-(4-methoxy-4'-(α-methylstilbene)oxy)]-1-(trifluoromethyl)-trifuoroethoxy)-1-[2-(ethyloxy)ethoxy]-2,2,3,3-tetrafluoropropane (22)

22 was synthesized as described in detail in a previous publication from our laboratory.[5]

Polymerizations

All polymerizations were initiated with $EtAlCl_2$ which generates the proton from traces of water available in CH_2Cl_2. Me_2S was used as Lewis base (Table I). Additional experimental details are presented elsewhere.[5]

Techniques

All monomers and polymers were characterized by a combination of techniques consisting of 200 MHz ^{1}H-NMR spectroscopy, gel permeation chromatography (GPC, polystyrene standard), high pressure liquid chromatography (HPLC), differential scanning calorimetry (DSC, 20°C/min) and thermal optical polarized microscopy. Experimental details are presented elsewhere.[2]

RESULT AND DISCUSSIONS

The synthesis of monomers 4, 13, 17 and 22 is outlined in Schemes I to IV. Polymerization results are summarized in Table I.

Table I: Polymerization of Vinyl Ether Monomers. Polymerization solvent, CH_2Cl_2; Polymeriztion temperature, 0 °C.

Monomer(s)	Monomer conc., $[M]_o$ (mol/l)	$[Me_2S]_o$/ $[EtAlCl_2]$ (mol/mol)	$[M]_o$/ $[EtAlCl_2]_o$ (mol/mol)	Reaction time(h)	Polymer		
					yield(%)	Mn(g/mol)	Mw/Mn
4	0.08	124	6.7	4.0	95	4700	1.22
13	0.08	124	6.7	2.0	88	6000	1.17
4/13(1/1)	0.08	124	6.7	4.0	79	3400	1.22
17	0.07	124	6.7	4.0	83	8300	1.07
22	0.09	19.3	10.0	4.0	60	6900	1.07

As we can see from this Table, all monomers, regardless of the functional group present in their molecule, lead to polymers with narrow molecular weight distribution. The goal of this report was not to demonstrate their living cationic polymerization, but only to see the variety of functional groups present in these monomers that can be tolerated by this cationic polymerization technique. The narrow molecular weight distributions obtained are however an excellant indication that all these monomers may be polymerizable through a living mechanism. Previous papers from this series have demonstrated that vinyl ethers containing 4-cyanobiphenyl mesogenic groups and various spacer length polymerize by a living mechanism.[3-5]

The thermal characterization of the resulting polymers is presentd in Table II. With the exception of poly(4) which exhibits a monotropic s_A mesophase which can be detected only by optical microscopy, all other polymers display enantiotropic s_A mesophases. It is very interesting to observe that poly(13) does not exhibit side chain crystallization. To our knowledge this may represent one of the very few if not the only noncrystallizable side chain liquid crystalline polymer based on a terminally attached mesogenic group, a spacer containing eleven methylenic units and a flexible backbone.[6]

Table II; Thermal Characterization of Poly(vinyl ether)s. Data on the first line refer to the first heating scan and on the second line to the second heating scan.

Polymer	Thermal transitions (°C) and corresponding enthalpy changes (kcal/mru)	
	heating	cooling
poly(4)	k 50.0 (0.18) k 129.8 (5.87) i k 131.1 (5.48) i	i 113.1 (5.20) k
poly(13)	g 1.7 s_A 105.3 (0.51) i g -0.4 s_A 104.1 (0.51) i	i 98.3 (0.43) s_A 0.4 g
poly(4/13)(1/1)	k 64.9 (2.24) k 127.6 (1.23) s_A 147.2 (1.02) i k 39.2 (0.13) k 127.0 (1.10) s_A 148.3 (0.63) i	i 138.2 (0.56) s_A 119.0 (0.92) k 33.1 (0.04) k
poly(17)	k 47.3 (2.58) k 68.8 (1.66) s_A 153.3 (0.66) i k 20.1 (0.39) k 52.9 k 67.6 (2.91) s_A 148.4 (0.64)i	i 141.7 (0.58) s_A 19.4 (1.55) k
poly(22)	k 53.9 (3.19) s_A 67.2 (0.17) i g 44.2 k 53.7 (2.82) s_A 68.5 (0.30) i	i 55.0 (0.38) s_A 34.8 (2.66) k

a) a monotropic s_A mesophase is observed on the optical microscope between 112 °C and 118 °C

These experiments are demonstrating that cationic polymerization of mesogenic vinyl ethers provides one of the most reliable synthetic methods which can be used in the molecular engineering of side chain liquid crystalline polymers. Cationic polymerization performed with nonnucleophilic counterions and Lewis base can tolerate functionalities like: nucleophilic aromatic groups, nitro and cyano groups, aromatic esters, double bonds and acidic protons.

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