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Synthesis and characterization of liquid crystalline poly(p-vinylbenzyl ether)s

Virgil Percec*, Jose M. Rodriguez-Parada[a], and Cecilia Ericsson[b]

Department of Macromolecular Science, Case Western Reserve University,
Cleveland, OH 44106, USA

SUMMARY

The synthesis and characterization of poly(p-vinylbenzyl ether)s containing 4-oxybiphenyl or 4-oxy-4'-methoxybiphenyl mesogens or a 4-oxy-4'-methoxybiphenyl mesogen which is connected to the benzyl ether group through one, two or three oligo(oxyethylene) units, are presented. The first two polymers exhibit a nematic mesophase while the last three a highly ordered smectic mesophase.

INTRODUCTION

The synthesis and characterization of both main-chain (1-6) and side-chain (7-9) thermotropic liquid crystalline polymers (LCP) containing oligo-(oxyethylene) units as spacers has received considerable interest especially because the ether-linked spacers are more flexible than the homologues alkane spacers. Our interest in LCP containing oligo(oxyethylene) spacers is mostly due to our interest in LC polypodants which can lead to liquid crystalline host-guest systems (6). Side-chain LCP containing oligo(oxyethylene) spacers exhibit a pseudo-crown-ether structure and therefore they represent a simple approach to the synthesis of LC polypodants. A major requirement in achieving this goal for side-chain LCP is the synthesis of polymers exhibiting a low degree of order in the mesomorphic phase (i.e., nematic, smectic A or smectic C), and at the same time, hydrolytic stability, particularly under nucleophilic conditions.

The goal of this paper is to present the synthesis and characterization of a series of LC poly(p-vinylbenzyl ether)s containing oligo(oxyethylene) spacers. To our knowledge, these polymers represent the first examples of liquid crystalline p-substituted polystyrenes.

EXPERIMENTAL

A. Synthesis of Monomers and Polymers

Scheme 1 outlines the synthesis of the described monomers and polymers. The preparation of 4-methoxy-4'-hydroxybiphenyl and its alcohol derivatives has been reported elsewhere (8). p-Chloromethylstyrene was prepared as previously reported (10). All p-vinylbenzyl ethers were synthesized by the phase transfer catalyzed Williamson etherification of the corresponding alcohol or phenol with p-chloromethylstyrene in THF at room temperature. An example of this procedure is given as follows. 4-Methoxy-4'-(2-hydroxyethoxy)biphenyl (1.0 g, $4.1\mathrm{x}10^{-3}$mole), p-chloromethylstyrene (0.75 g, $4.9\mathrm{x}10^{-3}$ mole) and tetrabutylammonium hydrogen sulfate (TBAH, 0.28 g, $8.2\mathrm{x}10^{-4}$mole) were dissolved in 70 ml of THF and 20 ml of 50 weight % aqueous NaOH were

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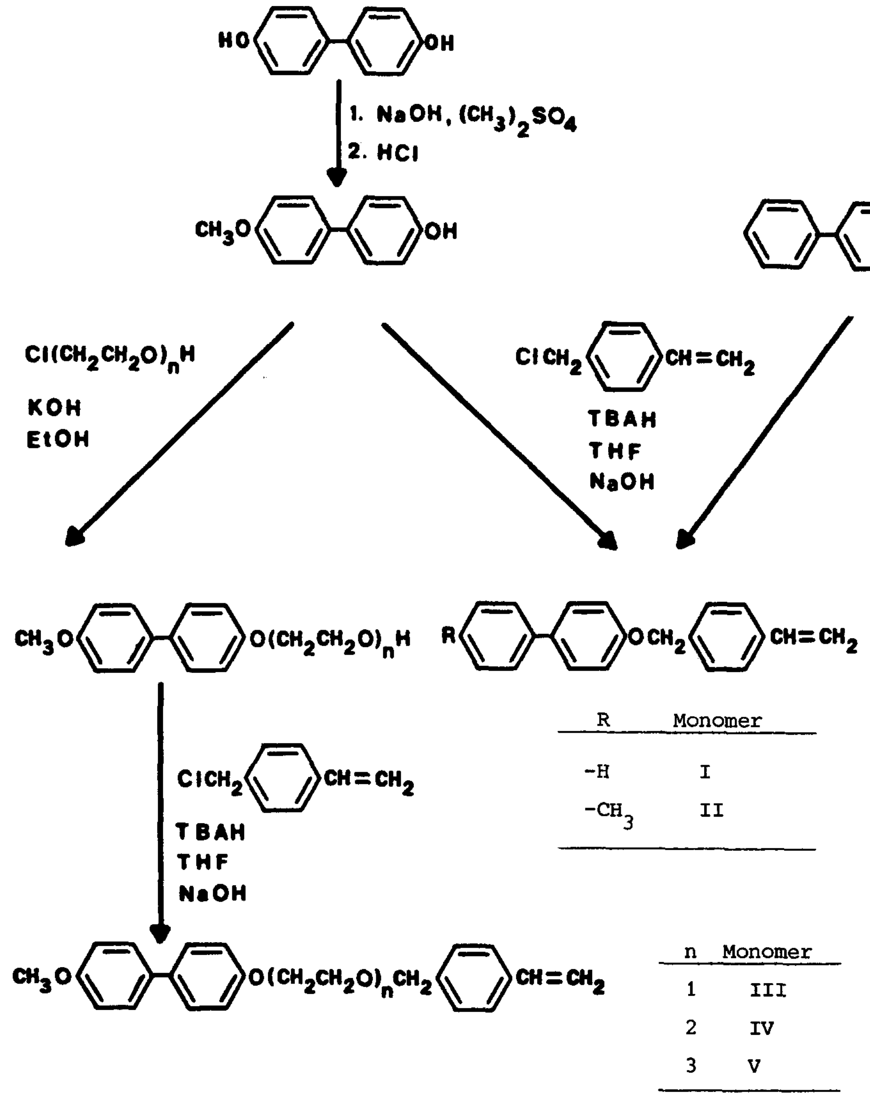
* To whom offprint requests should be sent

Present Adresses: [a]Max-Planck-Institut für Polymerforschung, D-6500 Mainz, FRG; [b]Department of Polymer Technology, Royal Institute of Technology, Stockholm, Sweden added. The reaction mixture was stirred at room temperature for 15 hrs, and then the organic phase was separated and poured into water. The precipitated product was filtered and dried under vacuum at room temperature. It was further purified by recrystallization from a mixture of benzene/cyclohexane (50/50, V/V) to yield 1.68 g (68%) of white crystals. m.p. = 166-168°C. Monomers IV and V were separated from the reaction mixture by evaporating the THF in a rotavapor at room temperature. These two monomers were recrystallized from methanol.

Table I summarizes the melting points and the chemical shifts of the 200 MHz ^{1}H-NMR spectra ($CDCl_3$, TMS) of all monomers.



R	Monomer
-H	I
$-CH_3$	II

n	Monomer
1	III
2	IV
3	V

Scheme 1: Synthesis of p-vinylbenzyl ether monomers

Table I: Characterization of p-vinylbenzyl ether monomers

Monomer	m.p. (^{o}C)	200 MHz ^{1}H-NMR (δ, ppm)
I	166-168	5.10 (s, Ph-C$\underline{H}_2$O-), 5.24 and 5.77 (d, =C$\underline{H}_2$), 6.74 (d of d, -C$\underline{H}$=), 7.0-7.6 (m, 13 aromatic protons)
II	186-188	3.82 (s, C$\underline{H}_3$O-), 5.09 (s, Ph-C$\underline{H}_2$O-), 5.23 and 5.77 (d, =C$\underline{H}_2$), 6.71 (d of d, -C$\underline{H}$=), 6.9-7.5 (m, 12 aromatic protons)
III	130-131	3.83 (s, C$\underline{H}_3$O-), 3.88 (t, -C$\underline{H}_2$O-), 4.17 (t, -C$\underline{H}_2$OPh), 4.60 (s, Ph-C$\underline{H}_2$O-), 5.23 and 5.71 (d, =C$\underline{H}_2$), 6.69 (d of d, -C$\underline{H}$=), 6.9-7.5 (m, 12 aromatic protons)
IV	80-95	3.61-3.79 (m, two -C$\underline{H}_2$O-), 3.84 (s, C$\underline{H}_3$O-), 3.90 (t, -C$\underline{H}_2$O-), 4.16 (t, -C$\underline{H}_2$OPh), 4.55 (s, Ph-C$\underline{H}_2$O-), 5.21 and 5.72 (d, =C$\underline{H}_2$), 6.70 (d of d, -C$\underline{H}$=), 6.9-7.5 (m, 12 aromatic protons)
V	60-63	3.57-3.75 (m, four -C$\underline{H}_2$O-), 3.83 (s, C$\underline{H}_3$O-), 3.88 (t, -C$\underline{H}_2$O-), 4.13 (t, -C$\underline{H}_2$OPh), 4.53 (s, Ph-C$\underline{H}_2$O-), 5.21 and 5.71 (d, =C$\underline{H}_2$), 6.68 (d of d, -C$\underline{H}$=), 6.9-7.5 (m, 12 aromatic protons)

All monomers were polymerized in dried dioxane by using AIBN as a radical initiator at 60^{o}C for 15 hrs. Polymerizations were carried out in Schlenk tubes under an argon atmosphere after the monomer solutions had been degassed. The monomer concentration was 10% (w/V) and the initiator concentration was 1 wt% versus the monomer. After the polymerization time, the reaction mixture was diluted with THF and then precipitated into methanol. The filtered polymers were dried under vacuum and then purified by reprecipitation from THF solutions into methanol. The characterization of all the resulting polymers is presented in Table II.

B. Techniques

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All polymers were characterized by differential scanning calorimetry (20^{o}C/min), optical polarization microscopy, and gel permeation chromatography (calibration based on polystyrene standards). The experimental techniques and the instrumentation used were previously described (8). X-ray diffraction patterns were taken using CuKα radiation in an evacuated flat plate X-ray camera at room temperature. Film to sample distance was varried from 5 to 20 cm. Polymer samples were prepared by heating the polymer powders above the isotropization temperature in a hot stage and then cooling at 10^{o}C/min to room temperature. Films of about 0.5 mm thickness were used.

RESULTS AND DISCUSSION

Table II presents the radical polymerization results and the thermal transitions of the polymers, together with their thermodynamic parameters. Although monomers I and II do not have a spacer in between the polymerizable group and the mesogenic unit, their corresponding polymers exhibit a nematic mesophase. Both, poly(I) and poly(II) present very low enthalpies of isotropization on the heating scans. On the cooling scans, no ethalpy change associated with the isotropization transition could be observed, although optical polarization microscopy revealed the formation of the mesomorphic phase almost at the same temperature as it disappeared on the heating scan. Side-chain LCP without spacers in between the main-chain and the mesogenic unit have been previously encountered (11, 12). Nevertheless, poly(I) seems to represent only the second example of LCP based on 4-hydroxybiphenyl, the first one being poly(p-biphenyl acrylate) (13) which exhibits a smectic mesophase.

Table II

Radical polymerization of monomers and characterization of the polymers

Monomer	Conv. (%)	$\bar{M}n\times10^{-3}$ (GPC)	$\bar{M}w/\bar{M}n$	Thermal Transitions and Thermodynamic Parameters[a)]					
				Heating			Cooling		
				Tg	Tl/ΔHl	Ti/ΔHi	Ti/ΔHi	Tl/ΔHl	Tg
I	55	12.0	1.88	97	-	182/0.21	-	-	90
II	70	5.7	3.81	-	183[b)]/4.04	233/0.15	-	169/4.81[c)]	-
III	30	12.5	1.75	-	-	142/6.12	125/5.55	-	-
IV	55	12.4	1.78	57	-	104/4.16	80/3.72	-	-
V	49	11.2	1.71	30	-	85/4.41	57/3.85	-	-

a) Tg, Tl and Ti are in °C; ΔHi in kcal/mru; mru = mole repeat unit;
b) unidentified transition; c) overlapped transitions: ΔHi = ΔHi + ΔHl.

Considering our previous results on the use of benzyl ether type mesogenic units in side-chain LCP (14), the structure of poly(I) and poly(II) could be considered as being a polyethylene containing the benzyl ether of 4-hydroxybiphenyl and 4-hydroxy-4'-methoxybiphenyl, respectively, as mesogenic units, and not of a p-substituted polystyrene.

The polymers obtained from the monomers III, IV and V exhibit highly ordered smectic mesophases, similar to those reported for the corresponding polymers obtained from methacrylates, acrylates or propenyl ether monomers (8, 9). A typical texture for these polymers is shown in Figure 1.

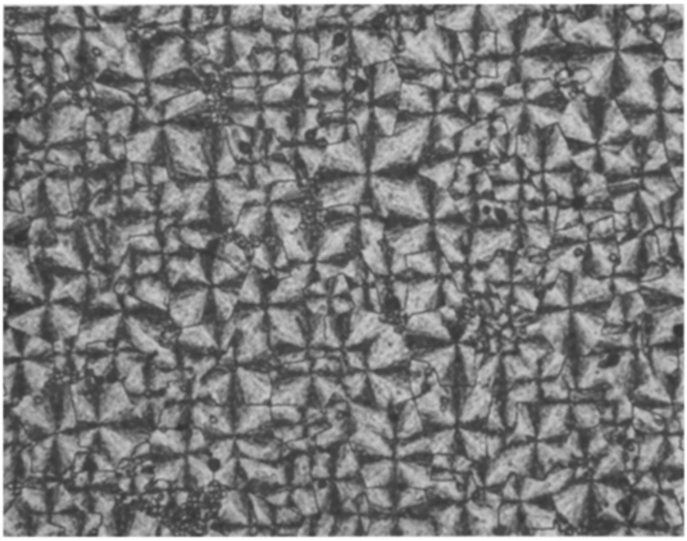


Figure 1: Optical polarization micrograph of poly(IV): cooling cycle, 104°C, magnification 300x, annealed for 24 hrs.

The X-ray diffraction data for these polymers and for poly(II) are presented in Table III.

Table III: X-Ray diffraction data of polymers

Polymer	d-Spacing in Å for the observed reflexions$^{a)}$				
	Layer		Intra-layer		
Poly(II)	-	-	4.50(s, broad)		
Poly(III)	25.1(s),	12.6(m)	4.50(s),	3.98(m),	3.22(w)
Poly(IV)	28.5(s),	14.4(m)	4.48(s),	3.95(m),	3.15(w)
Poly(V)	32.4(s),	16.1(m)	4.50(s),	3.91(m),	3.16(w)

a) s= strong, m=medium, w=weak

They all show two equidistant sharp reflections in the small-angle region corresponding to the smectic layer, and three sharp reflections in the wide-angle region which are the same, within experimental error, for all the polymers.

The smectic layer spacing increases proportionally with spacer length and corresponds approximately to the length of one monomer unit, suggesting a single-layer or an interdigitated double-layer arrangement of the pendant side-groups. The same conclusion was reached previously for a polymethacrylate containing the same mesogen and a di(ethylene oxide) spacer (15). Furthermore, the wide-angle reflections for these polymers agree quite well with those reported for this polymethacrylate (15), suggesting a similar structure which was characterized as smectic E. Therefore, it seems that oligo(oxyethylene) spacers are stabilizing a mesomorphic structure which is independent of the nature of the polymer backbone, suggesting a very good decoupling of the mesogens and backbone.

These preliminary results on poly(p-vinylbenzyl ether)s containing mesogenic units attached directly or through flexible spacers, are providing a novel synthetic avenue for the preparation of side-chain liquid crystalline polymers.

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