Synthesis and characterization of oxyethylene copolymers with phenyl and/or 4,4'-biphenyl structural units in the backbone

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Summary

This paper describes the synthesis and characterization of a new series of copolymers with a predominantly poly(ethylene oxide) (PEO) backbone and phenyl and/or 4,4'-biphenyl structural units. Three copolymers, poly[oxyethylene]/poly[oxyphenylene] copolymer (**1**), poly[oxyethylene]/poly[oxybiphenylene] copolymer (**2**), and poly[oxyethylene]/poly[oxyphenylene]/poly[oxybiphenylene] copolymer (**3**), were prepared based on modifications of hydroquinone and/or 4,4'-biphenol copolymerized with dimesylates of various length poly(ethylene glycol)s (PEGs). Depending on their composition and chain length of PEGs used in the polymerization, the copolymers show liquid crystallinity or non-liquid crystallinity.

Introduction

Recently, there have been several approaches to combine liquid crystallinity with PEO, for example, either by introducing the mesogenic groups along a PEO backbone to give main chain liquid crystalline polymers [1-2] or by attaching the mesogens to a PEO backbone through a spacer to give a side chain liquid crystalline polymer [3]. Also salt complexes of PEO derivatives containing the alkyl side chains have been shown to form liquid crystalline structures above the side chain melting temperature [4]. These approaches have been used in an effort to improve the ionic conductivity of PEO-based polymer electrolytes by providing two-dimensional well-defined channels for ion mobility [1-6]. But most methods employed relatively high molecular weight telechelic PEO derivatives in synthesizing the liquid crystalline PEOs (especially, main chain type LCs), and from a synthetic point of view, it is difficult to introduce large amounts of mesogenic groups in the PEO backbone because the end groups of PEO of high molecular weight are not relatively reactive in the desired reaction. In addition, a systematic study on the dependence of liquid crystallinity on the composition and chain length of PEO units has not been reported so far, although it is expected that the PEO copolymers show liquid crystalline behaviors with a relatively small content of PEO segments in the polymer backbone. In this study, we attempted to combine

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the various length PEO segments with the rigid oligophenylene moieties such as phenyl or 4,4'-biphenyl to establish the structure-property relationship of oxyethylene copolymers which have a mesogenic group and a flexible PEO spacer. The effect of the PEO chain length of the copolymers on their thermal and liquid crystalline properties was investigated in detail.

Experimental

Techniques

^{1}H-NMR (500-MHz) spectra were recorded on a Varian Unity Inova Spectrometer in $CDCl_3$ and with TMS as an internal standard. The thermal characterization of the polymer was carried out by differential scanning calorimetry (DSC) with a heating and cooling rate of 10 °C/min on a DSC TA 2910 instrument. Hot stage polarized light microscopy was carried out to examine the optical textures of the melts using a Nikon Optiphot-2 cross-polarizing microscope. Molecular weights were determined by gel permeation chromatography (GPC) with a Waters 515 LC instrument using THF as solvent and polystyrene as calibration standards.

Materials

All reagents were purchased from commercial sources (Aldrich or Lancaster) and used without further purification unless otherwise noted. Methylene chloride and DMF were dried over CaH_2 and distilled. PEGs were dried in vacuum before use.

PEG-dimesylates

The synthetic route to the PEG-dimesylates of various molecular weights is shown in Scheme 1, and only a representative example (i.e., PEG 200-dimesylates) is given here. In a 250 mL round-bottom flask were placed PEG 200 (5.00 g, 25 mmol), triethylamine (12.65 g, 125 mmol), and methylene chloride (125 mL). To this solution was added dropwise methanesulfonyl chloride (5.8 mL, 75 mmol) over 30 min at 0 °C. The mixture was stirred at room temperature under N_2 for 12 h. The reaction mixture was then poured into ice-cold water. The organic layer was separated and washed with aq HCl and water, respectively. The solvent was evaporated yielding a clean pale yellowish oil: Yield = 7.03 g (79 %); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.45 (m, -OCH$_2$CH$_2$OSO$_2$CH$_3$), 3.80 (m, -OCH$_2$CH$_2$OSO$_2$CH$_3$), 3.65 (m, -OCH$_2$CH$_2$O-), 3.10 (s, -OSO$_2$CH$_3$).

### General procedure for polymerization

Polymers (**1**-**3**) were prepared using the synthetic route shown in Scheme 2. To a 25 mL round-bottom flask equipped with a reflux condenser, a nitrogen inlet and outlet were added PEG-dimesylates (1.4 mmol), 4,4'-biphenol (1.4 mmol), anhydrous potassium carbonate (3.5 mmol), and fresh DMF (6 mL). Then the mixture was stirred at 140 °C for 24 h under N_2. The reaction mixture was then allowed to cool to room temperature and poured into water. The resulting solution was extracted with CH_2Cl_2. Evaporating the solvent gave dark brown viscous oil. The crude product was redissolved in $CHCl_3$ and the solution was poured into methanol. The precipitate was collected and vacuum dried. Polymer (**3**) was prepared using an identical method except that an

equimolar mixture of hydroquinone and 4,4'-biphenol was used instead of 4,4'-biphenol.

Results and discussion

Polymer synthesis

Dimesylates of various length PEGs were prepared by the reaction of methanesulfonyl chloride with the corresponding PEGs (Scheme 1) [7]. Before use in the polymerization, these dimesylates were purified thoroughly until their ^{1}H-NMR spectra corresponded to the expected structure. A series of copolymerization experiments of the PEG-dimesylates with hydroquinone and/or 4,4'-biphenol employing various reaction conditions was attempted resulting in twelve copolymers of different compositions (Scheme 2). Table 1 shows the copolymerization results, from which it can be found that the molecular weight of the copolymers increases as the higher molecular weight PEG unit was introduced.
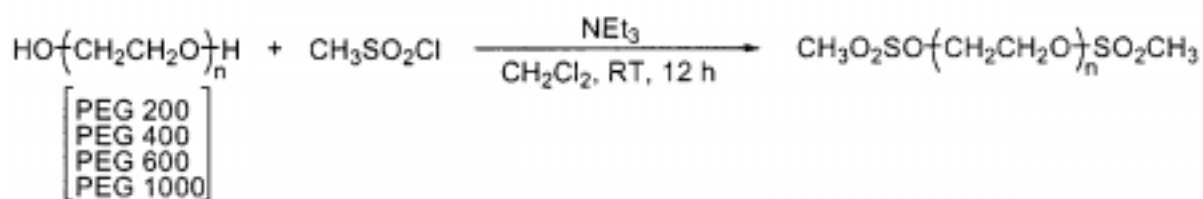
Scheme 1. Synthesis of PEG-dimesylates.
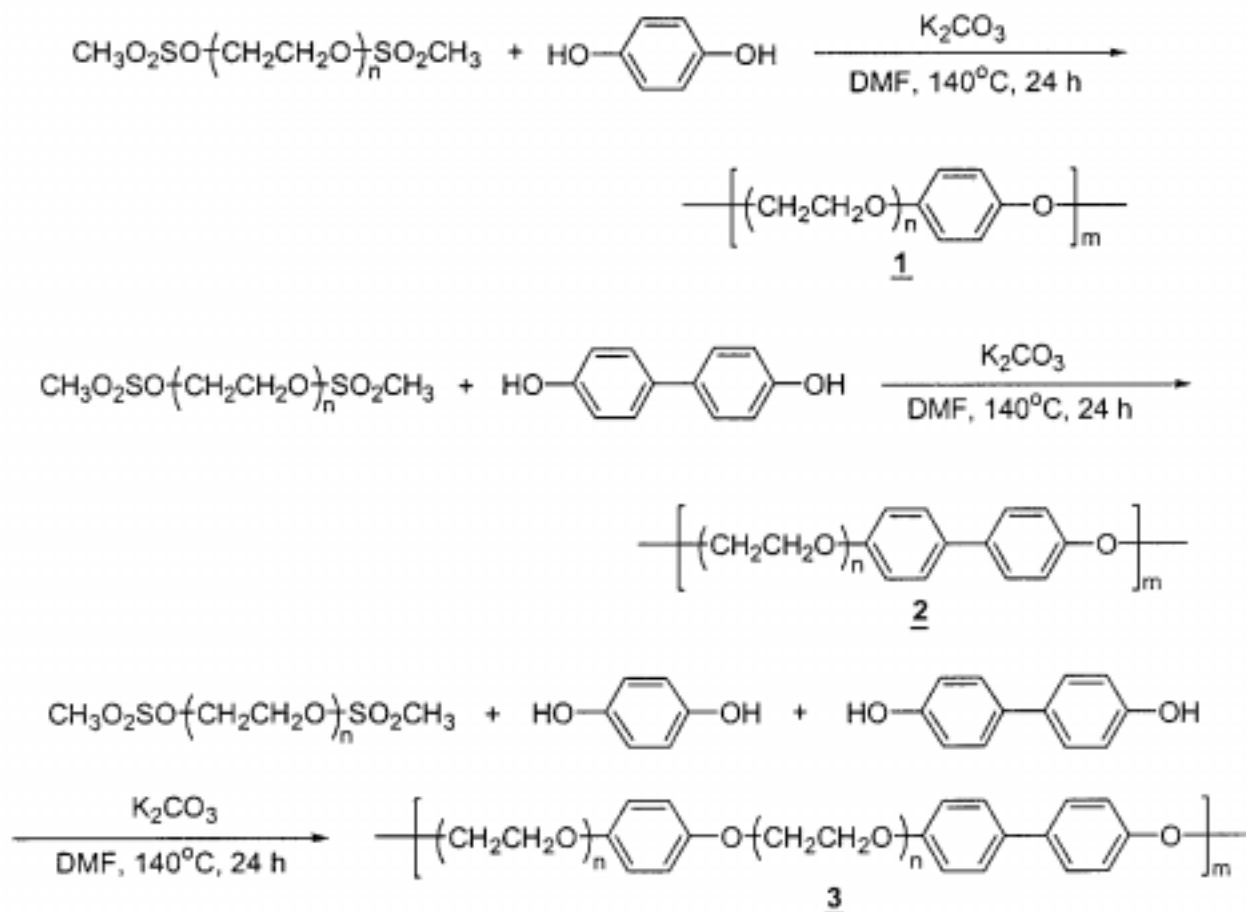
Scheme 2. Polymer Synthesis.

Table 1. GPC Results and Thermal Properties of Various Copolymers.

Entry	Code [a]	Yield (%)	$\overline{M_n}$	$\overline{M_w}$	MWD	T_g (°C)	T_m (°C)	T_i (°C)	$\triangle H_m$ (J/g)	$\triangle H_i$ [b] (J/g)
1	HQ-PEG 200	81	2,900	3,900	1.5	9.1	98	113	24.8	17.5
2	HQ-PEG 400	64	5,700	6,700	1.6	-21.3	49	-	36.1	-
3	HQ-PEG 600	54	7,100	8,200	1.5	-35.2	28	-	93.3	-
4	HQ-PEG 1000	36	9,800	17,400	1.7	-55.1	25	-	95.7	-
5	BP-PEG 200	85	3,500	4,800	1.6	10.3	101	113	22.8	16.1
6	BP-PEG 400	69	6,000	7,600	1.8	-23.2	46	-	31.6	-
7	BP-PEG 600	56	8,000	9,800	1.7	-34.8	29	-	92.4	-
8	BP-PEG 1000	48	13,000	20,000	1.9	-52.9	27	-	95.3	-
9	HQ/BP-PEG 200	79	3,500	4,600	1.7	8.7	98	108	25.2	19.7
10	HQ/BP-PEG 400	62	6,600	7,900	1.7	-26.1	43	-	34.1	-
11	HQ/BP-PEG 600	54	8,200	10,100	1.9	-35.2	27	-	94.7	-
12	HQ/BP-PEG 1000	32	11,400	20,000	1.8	-56.1	26	-	96.9	-

[a] Polymers are coded for example HQ-PEG 200. The code HQ and BP represent hydroquinone and 4,4'- biphenol, and the PEG units are coded by molecular weights. [b] Estimated from cooling scans.

In the case of the copolymerization of PEG 200-dimesylates with hydroquinone in DMF (Table 1, entry 1), the reaction mixture became very viscous under the given experimental conditions, and the stirring was impossible. However, the resulting molecular weight was low which implies that the low solubility of the polymer might determine the low polymerizability of the monomer. From the GPC trace of the resulting polymer, a clear bimodal molecular weight distribution was observed. In order to prevent the premature polymer precipitation, more solvent (DMF) was added to the reaction. Although this resulted in a substantial enhancement of the solubility of the polymer to give a monomodal molecular weight distribution, the additional solvent suppressed the polymerization resulting in a low molecular weight. Employing other comonomer systems such as 4,4'-biphenol and hydroquinone/4,4'-biphenol also resulted in low molecular weight (entries 5 & 9). However, using the dimesylates of PEG 400, PEG 600 and PEG 1000 instead of PEG 200 substantially enhanced the copolymerization with hydroquinone and/or 4,4'-biphenol to give much improved molecular weight of up to 13,000 (entry 8). It is likely that the given solvent system enhances the solubility of the growing polymer chain and base (K_2CO_3) in the reaction medium, thus preventing the premature precipitation of the polymer. The polymer obtained was not soluble in water and alcohol, but easily soluble in common solvents such as chloroform, THF and DMSO. The GPC traces of all of the resulting polymers show a monomodal molecular weight distribution (Figure 1). The 500 MHz ^{1}H-NMR spectra of PEG 200-dimesylates and the corresponding copolymer with 4,4'-biphenol are shown in Figure 2. It should be noted that no signals due to mesylates ($-OSO_2CH_3$) appeared at 3.10 ppm of the copolymer spectrum, and the ratio of peaks from the biphenyl moiety to those from the ethylene glycol segment was in good aggrement with a 1:1 copolymer structure.
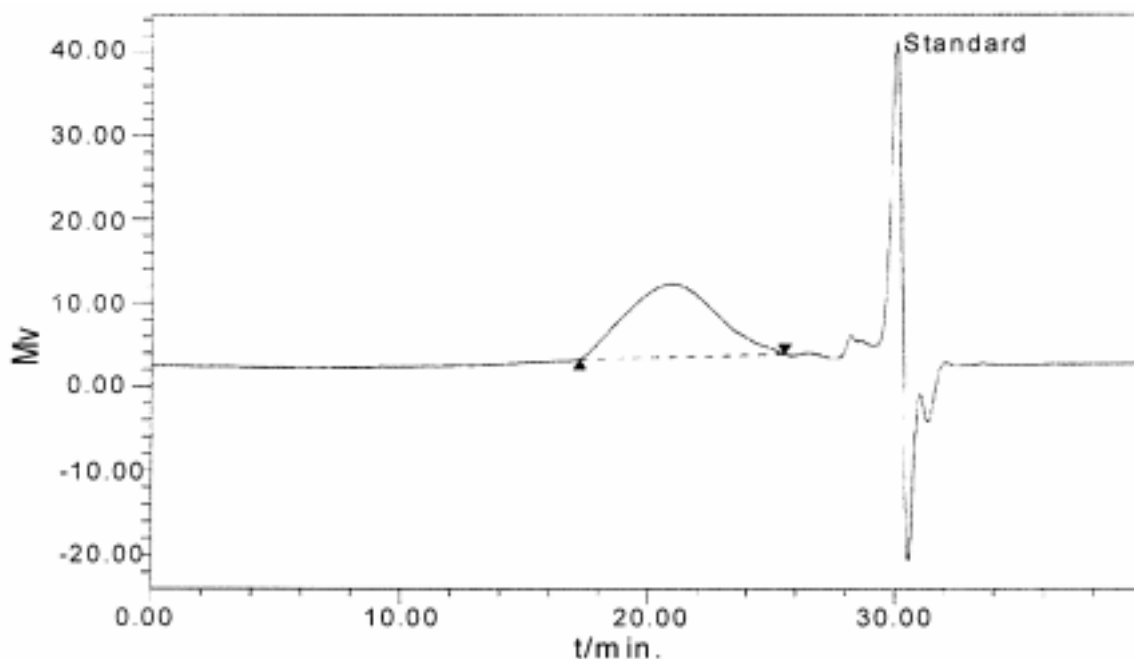

Figure 1. GPC trace of Copolymer BP-PEG 600 with $\overline{M_n}$ = 8,000 Relative to Polystyrene Standards.
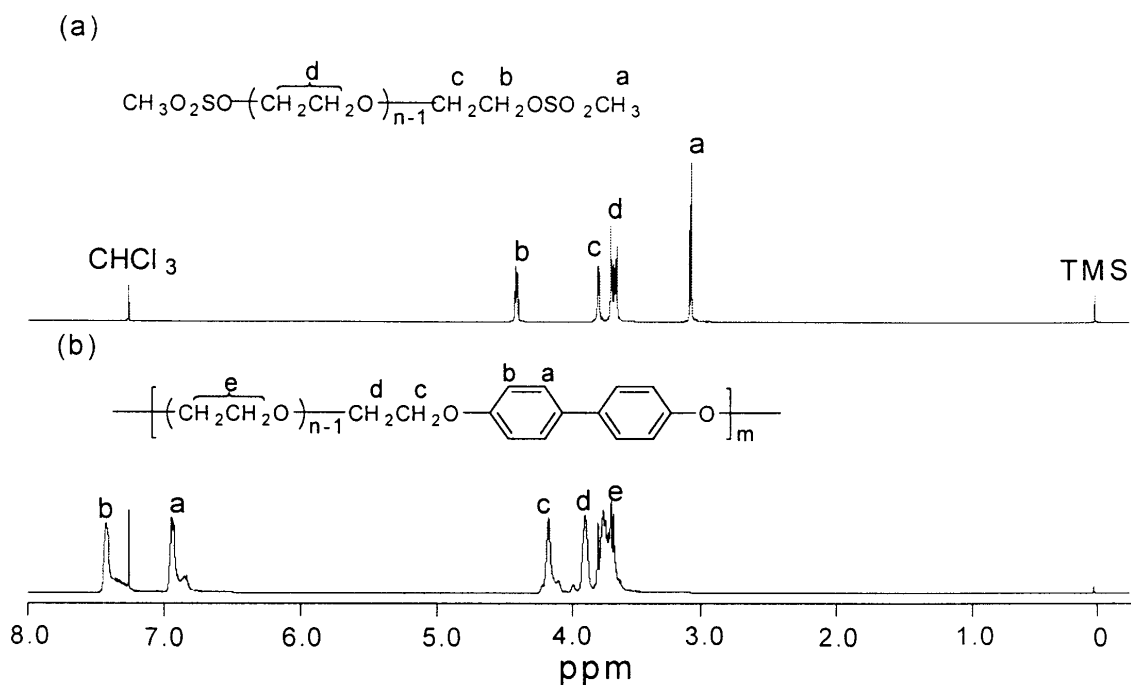
Figure 2. Typical ¹H-NMR Spectra of (a) PEG 200-dimesylates and (b) Copolymer BP-PEG 200.

Thermal characterization

The thermal properties of the copolymers of different compositions were studied by DSC and hot-stage polarized light microscopy. The representative DSC thermograms of the polymer (**2**) are shown in Figure 3, and the phase transition temperatures and enthalpies of various copolymers derived from DSC on second heating at a rate of 10 °C/min are shown in Table 1. The DSC trace exhibited by polymer **BP-PEG 200** showed two peaks indicating that there are two types of transformations: on the heating cycle, the polymer exhibited two endothermic peaks and on cooling, it showed the corresponding two exothermic peaks. It was found that the melting peak (Tm) is followed by a liquid crystalline phase culminating in a second endotherm prior to the onset of the clearing range at Ti. On cooling from the isotropic phase, a birefrigent texture, although weak and less well-defined, was observed when viewed through the polarized light microscope (Figure 4). However, it was not possible to obtain a clear characteristic texture which can be used to assign an unambiguous phase because of the very narrow temperature range of liquid crystalline phase. A similar liquid crystalline behavior was also observed in the sample of polymer **HQ-PEG 200** and **HQ/BP-PEG 200**, respectively. By comparison, all other samples with the longer PEG segments (MW= 400, 600 and 1000 g/mol) showed only a melting point from a crystalline to an isotropic phase. It was found that the copolymerization of higher molecular weight PEG-dimesylates with the corresponding comonomers results in decrease of melting temperature as expected, and the copolymers with the longest PEG segment have the highest enthalpy of fusion. The glass transition temperature is also decreasing with increasing length of the incoporated PEG segments. In summary, most of the materials prepared proved unsuccessful in giving liquid crystalline transition except the copolymers containing the PEG 200 segments.   The formation of liquid
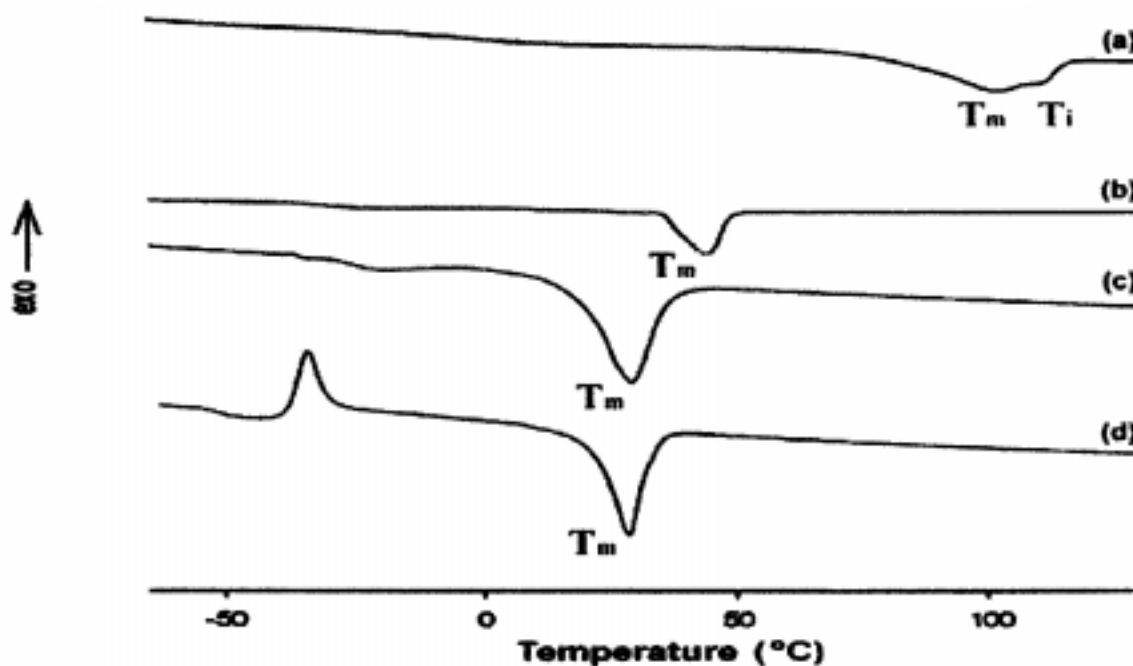
Figure 3. DSC Thermograms of Copolymers of Different Compositions at A Heating Rate 10°C/min: (A) BP-PEG 200, (B) BP-PEG 400, (C) BP-PEG 600, (D) BP-PEG 1000.
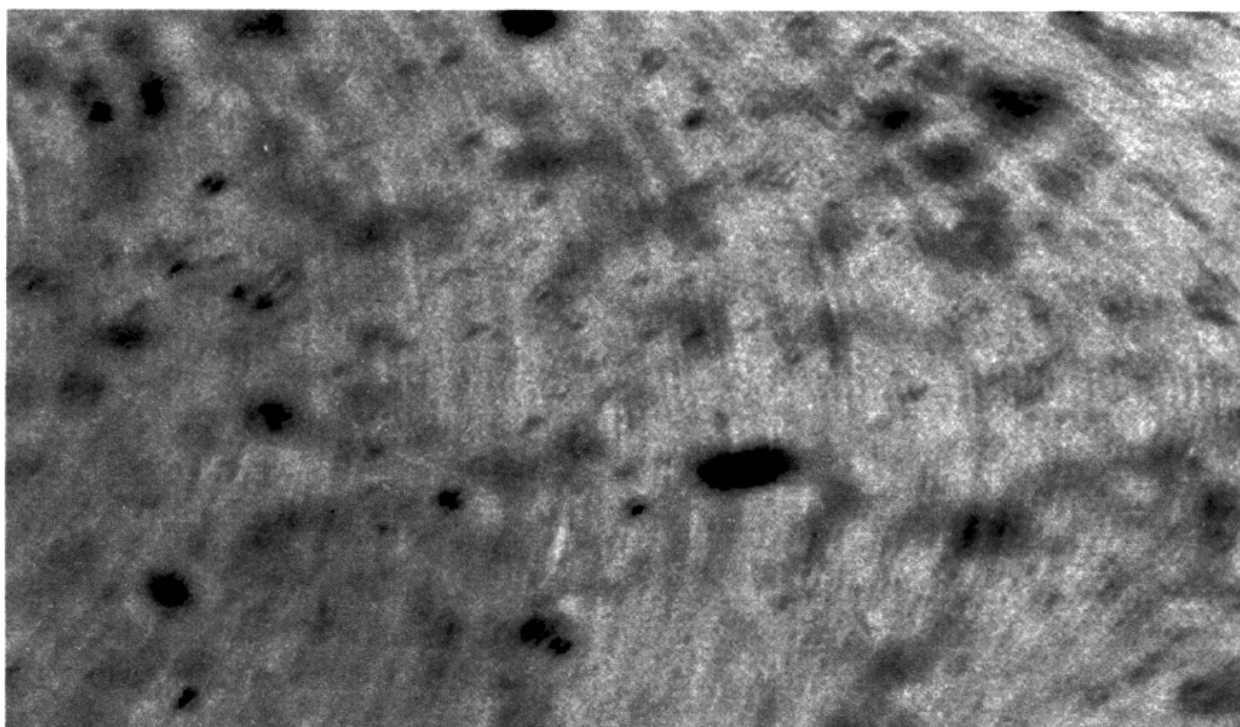

Figure 4. Optical Micrograph (crossed polars) of Copolymer BP–PEG 200 at 113 °C on cooling (magnification of ×1000).

crystalline phase for only copolymers containing PEG 200 segments may presumably be accounted for by the ordering of adjacent mesogens separated by a relatively shorter sequence of the skeletal oxyethylene units. Other copolymers of longer PEG segments (MW= 400, 600, and 1000 g/mol) seem not to be microphase separated due to the high content of oxyethylene units in the polymer.

In conclusion, new oxyethylene copolymers with phenyl and/or 4,4'-biphenyl structural units in the backbone have been prepared by reacting the hydroquinone and/or 4,4'-biphenol with dimesylates of PEGs of different molecular weights, and their liquid crystalline properties were evaluated: Liquid crystallinity is greatly influenced by the length of the PEG segment, and only polymers with short length PEG units (MW= 200 g/mol) are liquid crystalline over the narrow temperature range of ca. 10 °C.

Acknowledgements

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