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Synthesis and Structure of Thermotropic Main-Chain Polyethers Based on Bis(4-hydroxyphenoxy)-*p*-xylene

Håkan Jonsson, Per-Erik Werner,[†] Ulf W. Gedde, and Anders Hult*

Department of Polymer Technology, The Royal Institute of Technology, S-100 44 Stockholm, Sweden, and Department of Structural Chemistry, University of Stockholm, S-106 91 Stockholm, Sweden. *Received April 1, 1988; Revised Manuscript Received August 22, 1988*

ABSTRACT: Liquid-crystalline main-chain polyethers with methylol-linked mesogenic segments and methylene spacer groups of 7 to 12 carbons have been synthesized from bis(4-hydroxyphenoxy)-*p*-xylene and dibromoalkanes by using a phase-transfer-catalyzed Williamson ether synthesis. The molecular weights of the polyethers follow a distinct odd–even dependence (referring to the number of carbons in the spacer), most probably due to differences in solubility of the polymer during the polymerization. DSC and polarized light microscopy have revealed an odd–even dependence of the temperatures and enthalpy and entropy changes associated with crystal melting and isotropization. X-ray diffraction studies confirmed these observations in terms of a higher degree of order ("crystallinity") in polymers with an even-numbered spacer group. Polarized light microscopy revealed a number of different morphologies: negative banded and nonbanded spherulitic, positive nonbanded spherulitic, fan shaped, and mosaic, all indicative of a smectic mesomorphism. The experimentally found high values of the enthalpies and entropies of isotropization also indicate a smectic phase.

Introduction

The history of liquid-crystalline (LC) polymers started in 1956 when Flory[1] published a paper on concentrated polymer solutions. Flory stated that rigid-rod chain polymers, at a critical concentration, become liquid crystalline. Another milestone in this field was passed in 1975 when de Gennes[2] suggested that thermotropic main-chain LC polymers could be made by a combination of rigid and flexible units. In the same year, Roviello and Sirigu[3] synthesized the first polymer of this type by reacting *p*,*p*′-dihydroxy-α,α'-dimethylbenzalazine with acyl chlorides prepared from dicarboxylic acids of different lengths. Polyesters have been the most frequently made polymers in accordance with this concept (thoroughly reviewed by Ober, Jin, and Lenz in ref 4). LC polyethers, however, have been studied to a much lesser degree. Percec and Shaffer,[5] after performing extensive work on these polymers, state that the main advantages of LC polyethers over LC polyesters are lower melting temperatures, a broader mesophase stability range, and higher solubility.

The rigid (mesogenic) unit consists most often of a number of aromatic rings connected in the para position by a short link, which should be stiff in order to keep the aromatic rings in a linear arrangement. A great number of different links have been used, and esters are again the most common ones. A direct bond as in biphenyl,[6,7] an azo group,[8] and a stilbene group[9,10] are other examples of links that fulfill the condition mentioned above and give LC polymers. The rigid unit does not have to exhibit liquid crystallinity itself in order to be used as a mesogenic unit in a LC polymer.[11] It must, however, possess an appreciable amount of stiffness and, even more important, the molecule must be asymmetrical in shape.[12]

Following ideas from previous work carried out at the department,[13] a novel type of LC polyether has been synthesized by using diphenoxy-*p*-xylene segments as mesogenic units. This is the first example of a main-chain LC polymer that has methylol-linked mesogenic segments. A series of polymers with methylene spacers of different lengths have been synthesized and studied with IR, elemental analysis, thermal analysis (DSC,TMA), X-ray diffraction (WAXS), and hot-stage polarized light microscopy.

Experimental Section

Materials. Solvents and reagents were purchased from Aldrich and Merck and were used without further purification.

Characterization. Conformational and energy calculations were performed by using the MM2 (Molecular Mechanics Program Version 2) in Chem-X from Chemical Design LTD, Oxford (July 1987 update). ^{1}H NMR spectra were recorded on a 200-MHz Bruker spectrometer and IR spectra on a Perkin-Elmer 1710 infrared Fourier transform spectrophotometer. The number-average molecular weight (M_n) of the synthesized polymers was determined by elemental analysis of bromine (end-group analysis). Thermal transitions were recorded by differential scanning calorimetry (Perkin-Elmer DSC-2; 10 K/min scanning rate), hot-stage polarized light microscopy (Leitz Ortholux POL BKII equipped with Mettler Hot Stage FP 82 controlled by Mettler FP 80 Central Processor; 10 K/min scanning rate), and thermomechanical analysis (Perkin-Elmer TMA-1; 10 K/min heating rate, applying a pressure of 0.01 kg/mm^2 onto a penetration probe). The crystal and the liquid-crystal structures were determined by wide-angle X-ray scattering (WAXS) using a focusing Guinier-Hägg camera with transmission geometry. Strictly monochromatized Cu Kα1 radiation (λ = 0.154 059 8 nm) and single-coated films were used. The films were measured by a computer-controlled single-beam microdensitometer described in ref 14. The microstructures of 5–10-μm samples, as obtained directly after solvent casting and after heating above the isotropization temperature followed by cooling to room temperature, were recorded by polarized light microscopy (Leitz Ortholux POL BKII). Compensators were used to determine the birefringence of the microdomains.

Model Compound Synthesis. α,α'-Diphenoxy-*p*-xylene was synthesized as follows: To 55 mL of dry tetrahydrofuran, phenol (4.28 g, 45.5 mmol) and α,α'-dibromo-*p*-xylene (3.00 g, 11.4 mmol) were added. Potassium carbonate (6.28 g, 45.5 mmol) and a catalytic amount of 18-crown-6 were then added and the solution was heated to reflux. After 7 h the carbonate was filtered off and the filtrate poured into water. The precipitated crude product was filtered, boiled in 95% ethanol for a few minutes, and once again filtered. The precipitation procedure was repeated and gave tiny white needles as product. Mp 419 K. Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.8; H, 6.2; O, 11.1. Found: C, 82.6; H, 6.2; O, 11.6. IR: 3057, 3028, 2913, 2867, 1497, 1250, 1011, 803 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.06 (s, 4, CH$_2$), 6.95–6.99 (m, 6, Ar, ortho and para to OCH$_2$), 7.24–7.32 (m, 4, Ar, meta to OCH$_2$), 7.44 (s, 4, Ar, xylene unit).

Monomer Synthesis. Bis(4-hydroxyphenoxy)-*p*-xylene and 1,10-bis(4-hydroxyphenoxy)decane were synthesized according to a method described by Griffin and Havens.[15] The synthesis procedure for the former compound was as follows: To 35 mL of deaerated 95% ethanol, sodium dithionite (0.04 g, 0.23 mmol) was added. Hydroquinone (18.40 g, 167 mmol) was then added

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* To whom correspondence should be addressed.

[†] University of Stockholm.

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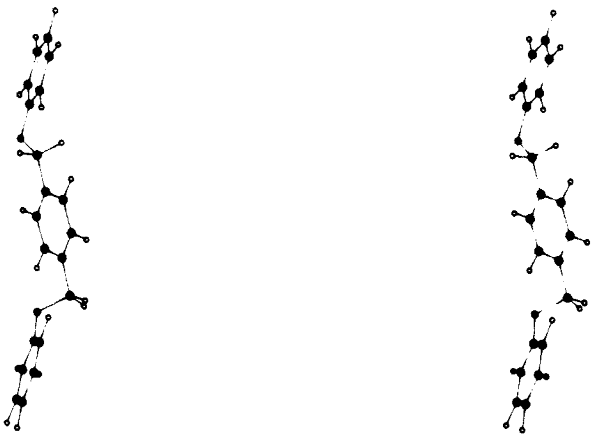


Figure 1. Stereoplot showing the conformation of α,α'-diphenoxy-p-xylene.

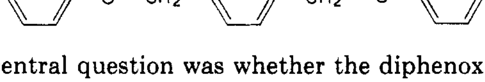
and dissolved by warming. α,α'-Dibromo-p-xylene (4.40 g, 16.7 mmol) was added and the solution was heated to reflux. Potassium hydroxide (2.81 g, 50 mmol) dissolved in 20 mL of 95% ethanol was then added dropwise over 25 min to the refluxing solution. After 4 h the solution was cooled slightly and acidified with 30% sulfuric acid. The alcohol-insoluble byproducts were filtered off, and the solvent was evaporated from the filtrate. The solid was washed with 500 mL of water and, after air drying, was recrystallized twice from 85% ethanol, which gave 1.0 g (19%) of small white crystals. Mp 514–517 K (slight decomposition). Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6; O, 19.9. Found: C, 74.2; H, 5.6; O, 19.9%. IR: 3376, 3074, 2908, 2865, 1515, 1246, 1016, 821 cm^{-1}. ^{1}H NMR (THF-d_8): δ 4.95 (s, 4, CH_2), 6.60–6.64 (m, 4, Ar, ortho to OH), 6.73–6.79 (m, 4, Ar, meta to OH), 7.38 (s, 4, Ar, xylene unit), 7.70 (s, 2, OH).

Data for 1,10-bis(4-hydroxyphenoxy)decane: Mp 424 K. Anal. Calcd for $C_{22}H_{22}O_4$: C 73.7; H, 8.4; O, 17.8. Found: C, 73.6;, H, 8.4; O, 17.4. IR: 3357, 3072, 2931, 2916, 2852, 1511, 1462, 1234, 1022, 827 cm^{-1}. ^{1}H NMR (THF-d_8): δ 1.35–1.68 (m, 16, CH_2), 3.80–3.86 (t, 4, OCH_2), 6.58–6.69 (m, 8, Ar), 7.86 (s, 2, OH).

Polymer Synthesis. A typical polymerization procedure for the α,ω-bis(bromoalkoxy) polyethers of bis(4-hydroxyphenoxy)-p-xylene (HPX) is as follows: To 7.5 mL of a 50% by weight sodium hydroxide solution, HPX (0.400 g, 1.24 mmol) was added. The suspension was heated to 85 °C under nitrogen and dibromododecane (0.407 g, 1.24 mmol) dissolved in 7.5 mL of o-dichlorobenzene was added. Finally, under intense stirring, tetrabutylammonium bromide (80 mg, 0.25 mmol) was added. After 7.5 h, the reaction mixture was acidified, washed with 2 M hydrochloric acid, and precipitated into methanol, and the polymer was then filtered off. The polymer was purified twice by dissolution in hot o-dichlorobenzene, followed by precipitation into acetone and methanol. Yield: 0.477 g (79%). Anal. Calcd: C, 77.2; H, 12.5; O, 8.2. Found: C, 76.1; H, 12.9; O, 8.1%. IR: 3069, 3050, 2919, 2851, 1510, 1466, 1244, 1031, 828 cm^{-1}.

Results and Discussion

Model Compound. The conformational characteristics of the anticipated mesogenic group (diphenoxyxylene unit) was investigated via the synthesis and conformational studies of a model compound, α,α'-diphenoxy-p-xylene.



The central question was whether the diphenoxyxylene unit could meet the following requirements (given in, e.g., ref 4) for a molecule to constitute a mesogenic segment in an LC polymer: (a) large aspect ratio; (b) anisotropic molecular polarizability; (c) rigidity and molecular parallelism (linear macroconformation).

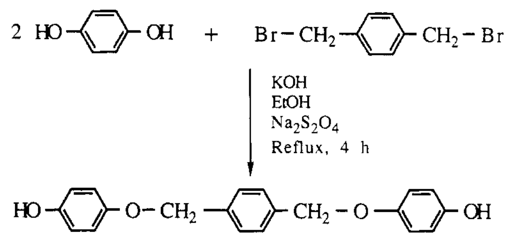


Figure 2. Synthesis of bis(4-hydroxyphenoxy)-p-xylene from hydroquinone and α,α'-dibromo-p-xylene.

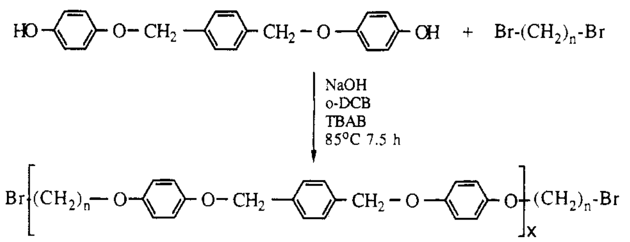


Figure 3. Synthesis of α,ω-bis(bromoalkoxy) polyethers of bis(4-hydroxyphenoxy)-p-xylene.

Criteria a and b are clearly fulfilled by a molecule which contain three para-phenylene groups and two oxygen atoms, and criterion c was also established by the use of computer-based conformational analysis. Figure 1 shows a stereoplot of the molecule; as can be seen, the outer phenylene rings lie in the same plane and thus give rise to molecular parallelism. The inner ring and the two methylene groups work as a large linking group that also stabilizes the molecule. The stabilization is due partly to the fact that large-scale rotation around the carbon–oxygen bond is inhibited by interaction between the methylene hydrogens and the two nearby hydrogens in the phenylene group. The energy required to move one of the outer rings from the position shown to a position that will make the molecule nonlinear (to the secondary energy minimum) is 16.2 kJ/mol.

Attempts to determine the dimensions of the unit cell of diphenoxyxylene by use of X-ray diffraction were not successful. It was, however, concluded that the cell is large and triclinic.

Thermal analysis (DSC) revealed only one first-order transition which was positively identified as crystal melting. The absence of one or more first-order transitions at higher temperatures demonstrates that the model compound does not possess liquid crystallinity. However, this does not mean that diphenoxy-p-xylene units are unsuitable as mesogens. In fact, most main-chain LC polymers are based on mesogenic units which are not in a mesomorphic state as monomers.[12]

Monomer and Polymer Synthesis. The nucleophilic monomer bis(4-hydroxyphenoxy)-p-xylene was synthesized from hydroquinone and α,α'-dibromo-p-xylene according to a method used by Griffin and Havens[15] for the synthesis of bis(4-hydroxyphenoxy)alkanes (Figure 2).

The polymers were made by a phase-transfer-catalyzed Williamson ether synthesis as described in the literature;[16–21] bis(4-hydroxyphenoxy)-p-xylene was polymerized with a dibromoalkane with tetrabutylammonium bromide as the phase–transfer catalyst (Figure 3). The two phases used were o-dichlorobenzene and an aqueous solution of sodium hydroxide. One major advantage of using this method for polyether synthesis is that only electrophilic chain ends are produced.[16,21–23] This is important since the presence of phenolic chain ends may hinder the formation of liquid-crystalline phases.[5]

The length of the dibromoalkane was varied between seven and 12 methylene units. Yields and molecular weights are listed in Table I. The notation HPX-C7 refers

Table I
Yield, Number-Average Molecular Weight, and Thermal Transitions of the Synthesized Polymers

			thermal transitns, K					
			heating				cooling	
polymer	yield, %	M_n	T_m	T_1	T_2	T_i	T_c	T_i
HPX-C7	86	8900	454	466		480	447	465
HPX-C8[a]	84	6800	473			493		
HPX-C9	88	9700	450	460		473	442	458
HPX-C10	81	7300	459	468		484	451	477
HPX-C11	84	10300	444	452	457	466	434	452
HPX-C12	79	7600	457	463	468	480	450	467
HPXB-C10[b]	83	7600						

[a] No transitions were recorded for sample HPX-C8 after the first heating scan due to thermal degradation. [b] Polymer HPXB-C10 was made by polymerizing bis(4-hydroxyphenoxy)decane with a benzylic bromide, i.e., α,α'-dibromo-p-xylene. The sample was thermally degraded during the first heating scan and no clear transitions could be recorded.

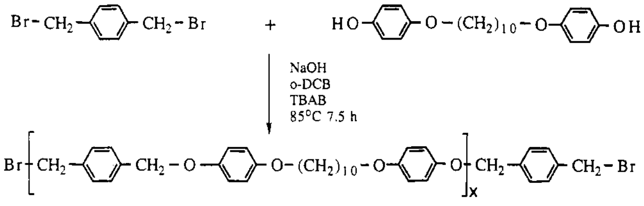


Figure 4. Synthesis of the polyether of bis(4-hydroxyphenoxy)decane and α,α'-dibromo-p-xylene.

to a polymer synthesized from bis(4-hydroxyphenoxy)-p-xylene and 1,7-dibromoheptane. Polymer HPXB-C10 was synthesized in a manner different from the other polymers. Instead of using bis(4-hydroxyphenoxy)-p-xylene as the nucleophilic monomer and polymerizing it with an alkylic bromide, bis(4-hydroxyphenoxy)decane was polymerized with a benzylic bromide, i.e., α,α'-dibromo-p-xylene (Figure 4). The structure of polymer HPXB-C10 is identical with that of polymer HPX-C10, except that HPXB-C10 has benzylic bromides as chain ends. This synthetic route was chosen in an attempt to increase the rate of reaction and the molecular weight of the resulting polymer through the use of a more reactive bromide in the polymerization step. According to Cameron and Law,[17] a fast system is preferable in order to obtain high molecular weight polymers within a reasonable time in phase-transfer-catalyzed reactions.

The polymers are soluble in hot solvents such as 1,1,2,2-tetrachloroethane, o-dichlorobenzene, and nitrobenzene. Polymers having an odd number of methylene units in the spacer have a higher solubility than those having even-numbered spacers. The solubility also tends to increase with increasing length of the spacer group. This is probably due to differences in the order of the different samples in the semicrystalline phase. As a result of this variation in solubility, the molecular weights of the polymers display a clear odd-even dependence (Figure 5). This demonstrates the importance of having a good solvent as the organic phase, in order to avoid precipitation and early termination of the growing chain, in a phase-transfer-catalyzed polycondensation. This molecular weight determining effect may also be the reason for the absence of any significant difference in molecular weight between samples HPX-C10 and HPXB-C10, despite the differences in reactivity between the monomers used.

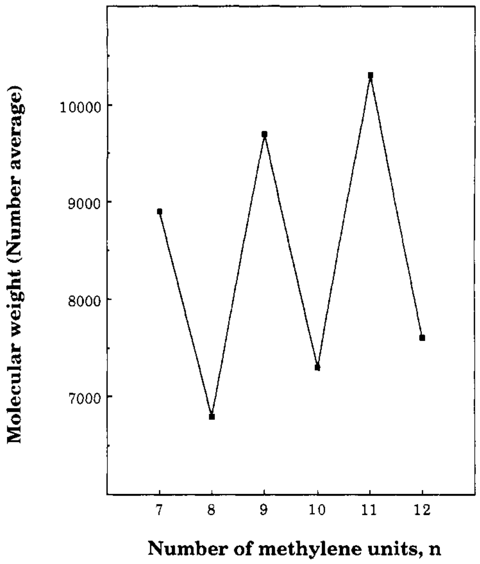


Figure 5. Molecular weight as a function of the number of methylene units in the spacer group.

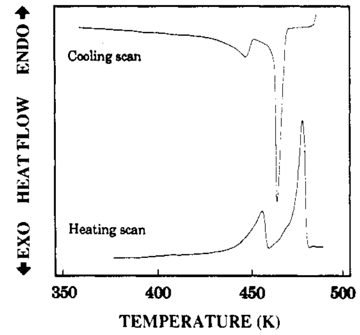


Figure 6. DSC thermogram of polymer HPX-C12. Second cooling and third heating scan.

Thermal Transitions. A typical DSC thermogram is shown in Figure 6 and all the thermal transitions are summarized in Table I. After the first heating all scans gave reproducible transitions. Only polymers having long spacers exhibited two minor first-order transitions at T_1 and T_2 in addition to the melting and isotropization transitions. The absence of detectable transitions in polymer HPX-C8 after the first heating scan is most probably due to thermal degradation of the sample. Above the isotropization peak an endothermic process was observed in all the polymers. This peak diminished on repeated heating without affecting the other peaks and is probably associated with the release of volatile low molecular weight species.

Polymer HPXB-C10, having benzylic bromine chain ends, was degraded in the first heating run and no clear transitions could be recorded. For polymer HPX-C10, having the same repeating unit, no such degradation was observed. The degradation of polymer HPXB-C10 must therefore be due to the lower stability of the chain ends, and indeed, there is a large difference in dissociation energy between a benzylic and a linear aliphatic C–Br bond, 230 kJ/mol[24] ($C_6H_5CH_2$–Br) and 289 kJ/mol[25] (C_3H_7–Br), respectively.

The thermal transitions show a very clear odd–even effect (Figure 7). Samples having an even-numbered spacer exhibit both higher melting and higher isotropization temperatures. The transition temperatures also decrease with increasing length of the spacer group. This odd–even dependence was first detected in LC polymers by Griffin and Havens[26] and in LC polyethers by Percec and co-workers.[10] The isotropization process was further verified by hot-stage polarized microscopy and the melting transition by TMA (Figure 7). The TMA experiments were performed on about 1-mm-thick specimens held in

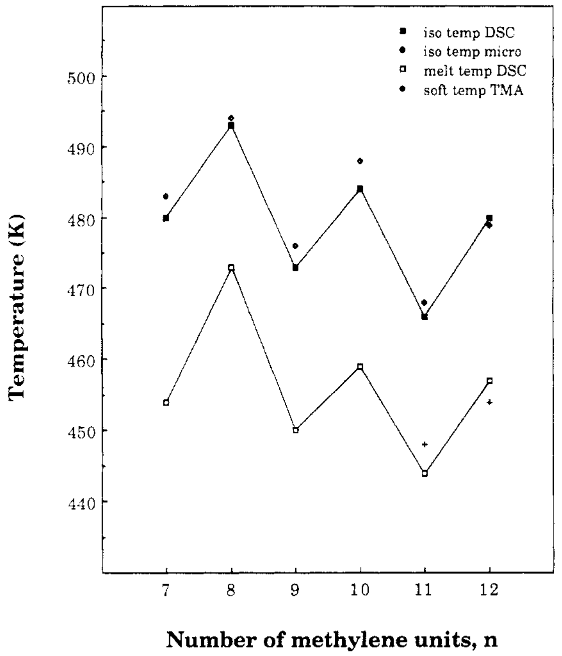


Figure 7. Temperatures for melting (T_m) and isotropization (T_i) as a function of the number of methylene units in the spacer group.

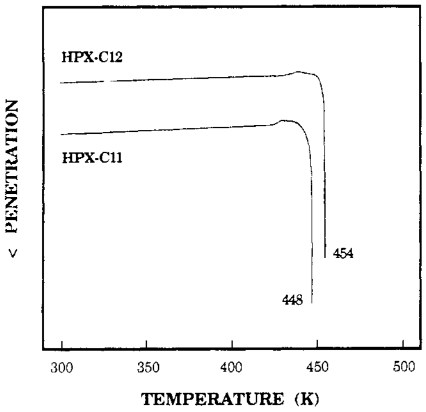


Figure 8. TMA curves of the two polymers HPX-C11 and HPX-C12 (penetration of 1-mm-thick specimens under a pressure of 0.01 kg/mm^2).

small aluminum containers. At the temperature indicated the probe fast and fully penetrated the specimen and thus proved the melting of the polymer (Figure 8).

When comparing melting and isotropization temperatures, as well as enthalpies and entropies, consideration must be given to the fact that they increase with increasing molecular weight.[4,21,22,27] However, in the present case there is a clear negative correlation between molecular weight and transition temperature (cf. Figures 5 and 7). Thus, for samples of the same molecular weight an even more pronounced odd–even effect would be observed.

Enthalpies and Entropies of Transition. In Table II the changes in enthalpies and entropies of melting and isotropization are summarized, and two main effects can be observed: (1) the values of ΔH and ΔS associated with isotropization are larger than those for melting; (2) the enthalpy and entropy changes associated both with melting and isotropization are larger for the even-numbered samples than for the odd ones. The first effect implies that the difference in order between the semicrystalline state and the mesophase is smaller than the difference between the mesophase and the isotropic melt. This indicates that the mesophases involved are highly ordered. The high values of the enthalpies and entropies may be taken as another indication supporting this assumption. Similar values have been found by Shaffer and Percec[7] in a thermotropic main-chain LC polyether (based on 4,4′-dihydroxybiphenyl and a dibromoalkane) possessing smectic mesomorphism. Ober et al.[4] state that polymers containing long spacers, about eight chain atoms or more, often display smectic mesophases.

Table II

Enthalpy and Entropy Changes of the Melting and Isotropization Transitions Calculated from DSC Thermograms, Together with the Crystallinity Index Determined from X-ray Diffraction Patterns[a]

polymer	ΔH_m	ΔH_i	ΔS_m	ΔS_i	crystallinity index
HPX-C7	9.0	24.1	19.7	50.3	0.33
HPX-C8[b]					0.40
HPX-C9	8.4	23.9	18.7	50.7	0.34
HPX-C10	15.7	26.8	34.3	55.3	0.40
HPX-C11	8.6	24.0	19.3	51.5	0.36
HPX-C12	19.6	37.7	42.8	78.6	0.40

[a] ΔH in kJ/mru and ΔS in J/mru·K (mru = moles of repeating unit). Enthalpy and entropy changes calculated from the second heating scan thermogram. [b] No registration in the DSC was possible for polymer HPX-C8 after the first heating scan due to thermal degradation.

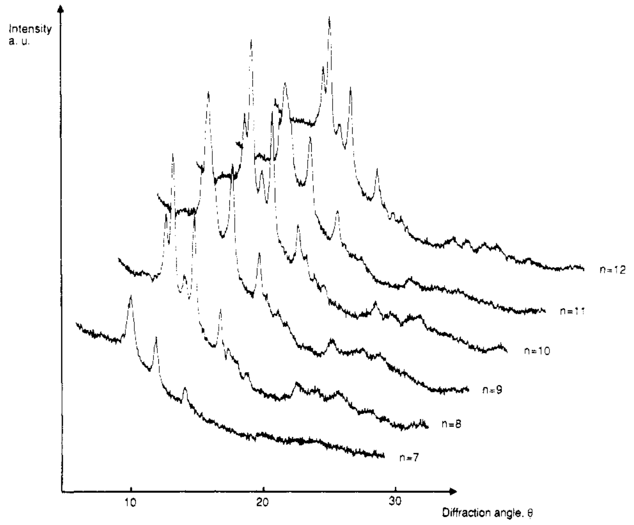


Figure 9. X-ray diffraction patterns of the synthesized polymers. Intensity as a function of the diffraction angle θ. The curves n = 8–12 are shifted along the x-axis.

The second effect, the well-known odd–even dependence, may be explained in terms of different degrees of order for polymers having odd or even numbers of methylene units in the spacer. The overall order in the semicrystalline state and in the mesophase is larger in the even-numbered samples than in the odd-numbered. The same observations has also been made by Krigbaum et al.,[27] Abe,[28] and Yoon and Bruckner[29] in LC polyesters.

Crystallinity Index. The assumption of different degrees of order between polymers having odd or even numbers of methylene units in the spacer is verified by the X-ray diffraction patterns shown in Figure 9. Crystallinity index data were determined on the basis of these diffraction patterns and the data are presented in Table II. The crystallinity index was calculated according to eq 1, in which A_c is the area of the sharp Bragg reflections

$$W_c = \frac{A_c}{A_c + A_a} \qquad (1)$$

corresponding to the crystalline part of the polymer and

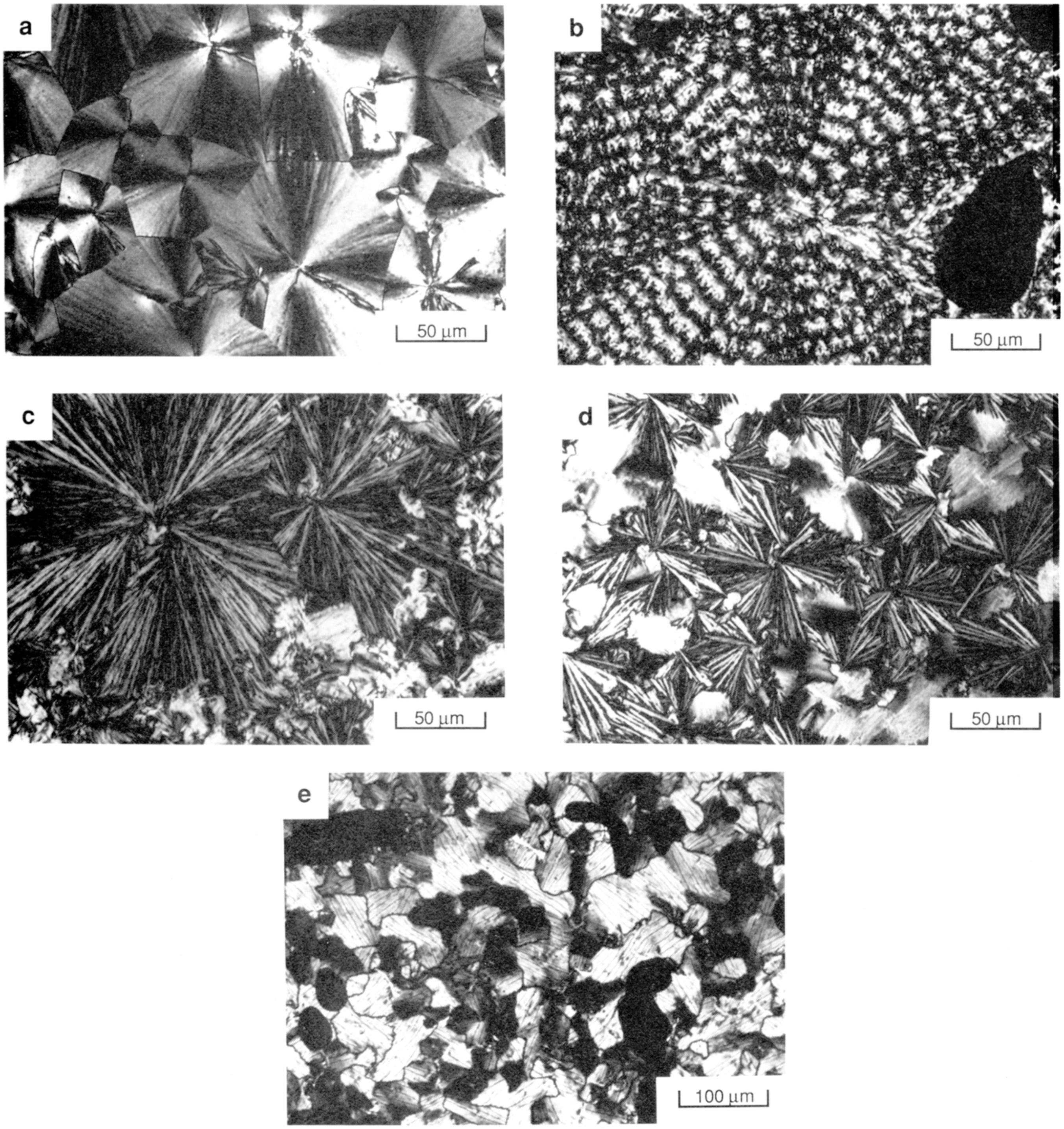


Figure 10. Polarized photomicrographs showing (a) a negative nonbanded spherulite, polymer HPX-C7, solvent casted; (b) a negative banded spherulite, polymer HPX-C7, solvent casted; (c) a positive spherulite, polymer HPX-C11, slowly (5 K/min) cooled from isotropic melt; (d) a fan structure, polymer HPX-C11, slowly (5 K/min) cooled from isotropic melt; and (e) a mosaic structure, polymer HPX-C9, air-quenched from isotropic melt.

A_a is the area of the broad amorphous peak.

It is evident that samples with a high ΔH_m (ΔS_m) also have a high crystallinity value. The Bragg spacings also show a clear and perfectly alternating odd–even dependence with odd-numbered polymers having spacings at 0.47, 0.45, 0.37, 0.32, and 0.23 nm and even-numbered polymers at 0.45, 0.43, 0.40, 0.37, 0.32, and 0.22 nm. As can be seen, the 0.40-nm spacing is not observed in the odd-numbered samples, indicating a different molecular arrangement of the polymer chains. Further X-ray work revealing the crystal structure of these polymers has been undertaken and will be presented in a future paper.

Morphological Studies. Thin films produced by solvent casting were studied in the optical microscope (equipped with crossed polarizers and in some cases a λ plate) as obtained (referred to as *solvent casted*) and after heating above the isotropization temperature followed by either quenching in air (approximate cooling rate, 200 K/min; referred to as *air-quenched*) or controlled cooling in the hot stage at a rate of 5 K/min (referred to as *slowly cooled*). A number of different structures were revealed in the samples and are described as follows.

1. Negative Nonbanded Spherulite (Figure 10a). This structure has a spherical optical symmetry and a lower refractive index along the radius of the spherulite. The chains are preferentially located in the tangential

Table III
Morphology As Revealed by Polarized Light Microscopy[a]

polymer	solvent casted	air-quenched	slowly cooled
HPX-C7	1	1	1 ,2
HPX-C8	imperfect 1	5	5
HPX-C9	3, 4, 5	5	5
HPX-C10	imperfect 1	5	5
HPX-C11	1 (minor degree), 5	5	3, 4, 5
HPX-C12	5	4, 5	5

[a] (1) Negative nonbanded spherulite; (2) negative banded spherulite; (3) positive spherulite; (4) fan structure; (5) mosaic structure.

plane of the spherulite.

2. Negative Banded Spherulite (Figure 10b). This structure is dissimilar to the aforementioned structure in that the refractive index ellipsoid (indicatrix) changes orientation periodically along the radius of the spherulite. In the optically isotropic domains the chains are preferentially oriented parallel with the light beam whereas in the optically anisotropic regions the chains are mainly located in the plane of the sample.

3. Positive Nonbanded Spherulite (Figure 10c). This spherically symmetric structure has a larger refractive index along the radius than in the transverse direction. The chain axis is thus mainly oriented along the radius. This structure is indicative of a smectic structure without order within the layers (smectic A or C).[30]

4. Fan Structure (Figure 10d). The refractive index is larger along the radius than in the transverse direction. This structure is very similiar to the aforementioned and indicates the presence of a smectic A or C phase.[30]

5. Mosaic Structure (Figure 10e). The mosaic domain is characterized by a uniform orientation of the refractive index ellipsoid. Cracks or striations parallel to the direction of high refractive index (i.e., chain axis) are present in all the mosaic domains. Disclinations of strength $\pm^1/_2$ have not been observed in domains with the mosaic structure. The mosaic structure displays all the characteristics of an ordered smectic structure, i.e., smectic B or G phase.[30]

The morphological observations made are summarized in Table III. The mosaic type of structure indicative of an ordered smectic phase (B or G) is displayed by all samples that have been heated above the isotropization temperature with the exception of the samples of polymer HPX-C7. Samples of polymer HPX-C11 display a "richness" of structures, which indicates the existence of both an "ordered" smectic phase (B or G) and a "disordered" smectic phase (A or C). Samples of polymer HPX-C7, the exception, display perfect negative spherulites. The elucidation of this "novel" type of liquid-crystalline structure requires further experimental work and will not be discussed further in this paper. In no sample was any change in microstructure observed when passing the crystallization temperature on cooling.

The formation of the smectic phases in samples of polymers HPX-C8 to HPX-C12 was further substantiated by hot-stage polarized microscopy studies of samples cooled from above the isotropization temperature to room temperature at a rate of 0.5 K/min. The formation of fibrous type of nuclei growing further both axially and perpendicularly forming the mosaic structure is very typical (Figure 11). The orientation of the chains is preserved during the growth of the mosaic domains. So-called "nematic droplets" were not observed in these samples. A very interesting observation was made in polymer HPX-C11, where the formation of the positive spherulites occurred at about 5 K lower temperature than that of the mosaic structure.

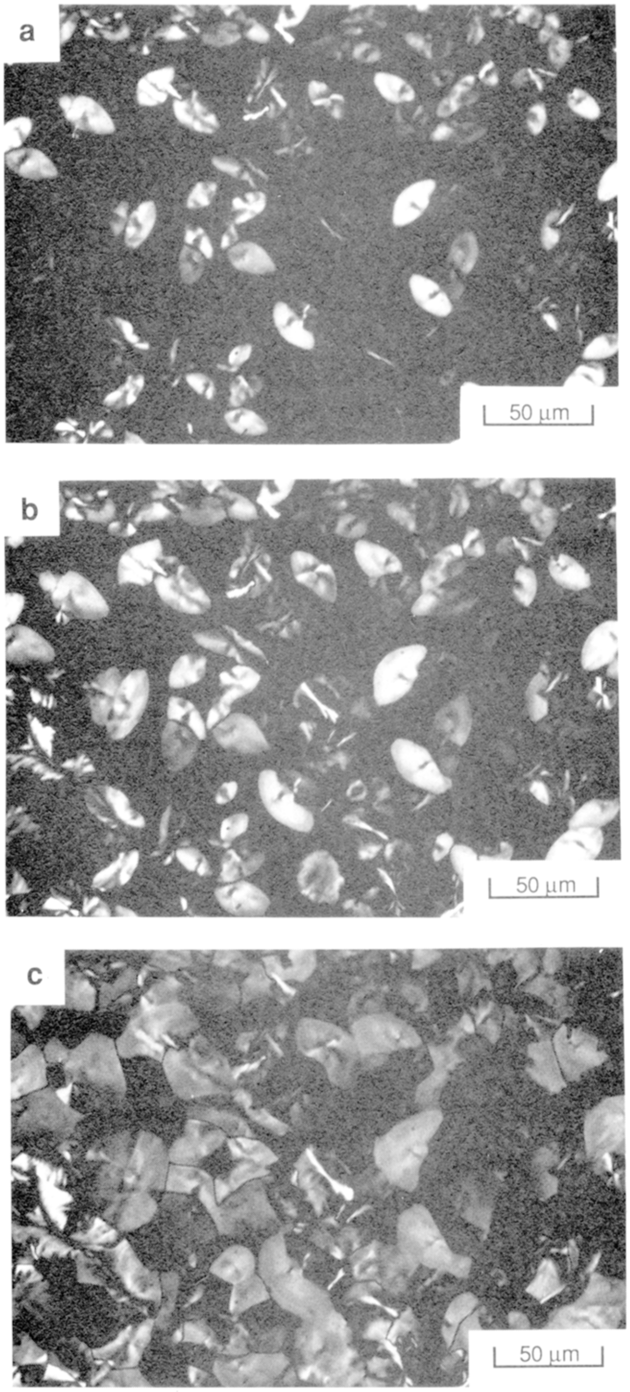


Figure 11. Polarized photomicrographs showing the formation of the mosaic structure in polymer HPX-C11 during a 0.5 K/min cooling from isotropic melt at (a) 460 K, (b) 455 K, and (c) 439 K.

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Registry No. (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH$)-($Br(CH_2)_7Br$) (copolymer), 117734-41-5; (4,4′,4″-

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$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br(CH_2)_7Br)$ (SRU), 117734-47-1; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br(CH_2)_8Br)$ (copolymer), 117734-42-6; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2O$-$C_6H_4OH)(Br(CH_2)_8Br$ (SRU), 117734-48-2; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br(CH_2)_9Br)$ (copolymer), 117734-43-7; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br$-$(CH_2)_9Br)$ (SRU), 117734-49-3; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br(CH_2)_{10}Br)$ (copolymer), 117734-44-8; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br$-$(CH_2)_{10}Br)$ (SRU), 117734-50-6; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br(CH_2)_{11}Br)$ (copolymer), 117734-45-9; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br$-$(CH_2)_{11}Br)$ (SRU), 117734-51-7; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br(CH_2)_{12}Br)$ (copolymer), 117734-46-0; (4,4′,4″-$HOC_6H_4OCH_2C_6H_4CH_2OC_6H_4OH)(Br$-$(CH_2)_{12}Br)$ (SRU), 117734-52-8; α,α'-diphenoxy-*p*-xylene, 10403-79-9; α,α'-dibromo-*p*-xylene, 623-24-5; phenol, 108-95-2; bis(4-hydroxyphenoxy)-*p*-xylene, 108196-53-8; 1,10-bis(4-hydroxyphenoxy)decane, 70856-53-0; hydroquinone, 123-31-9; sodium hydroxide, 1310-73-2; tetrabutylammonium bromide, 1643-19-2.

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First-Order Wetting Transitions of Polymer Mixtures in Contact with a Wall

I. Carmesin

Institut für Physik, Universität Mainz, Postfach 3980, Max-Planck-Institut für Polymerforschung, Mainz, Federal Republic of Germany

J. Noolandi*

Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, Canada.

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ABSTRACT: A binary mixture of polymers A and B in contact with a wall C is considered at coexistence. The system is isotropic in two directions and inhomogeneous in the direction d perpendicular to the surface. We study the polymer profiles within a selected range of two parameters, namely, the local chemical potential at the surface μ_1 and a parameter g which controls the strength of the attractivity of the surface. In order to study the system we carry out a mean-field self-consistent calculation of the polymer distribution functions, based on the biased diffusion equation, to account for the polymer–polymer and polymer–wall interaction energies, as well as the changes in the conformational and configurational entropies due to the presence of the surface. For the range of parameters considered, we find strong first-order wetting transitions. The limitations of the long-wavelength approximation to surface problems, developed earlier, are pointed out.

1. Introduction

A polymer mixture in contact with a wall at coexistence of both the A-rich and the B-rich phases shows wetting transitions depending on the interaction of polymers A and B with the wall. This means that a macroscopically thick layer at the wall can be found experimentally depending on the temperature, the chain length, the kind of polymers, and the nature of the surface. Theoretically the interaction of the polymers with the surface has been described by the local chemical potential μ_1 and a second parameter g controlling the attractivity of the surface.[1] One of us has earlier analyzed this problem in the long-wavelength limit of the Flory–Huggins approximation and found first-order wetting, critical wetting, and tricritical wetting.[2] This approach breaks down if one looks at the problem at low bulk concentration (here "bulk" means far away from the wall) of one of the components.[3] In this paper we make use of a more general mean-field approach starting from the functional integral representation for a polymer mixture, which does not suffer from the above limitation.[4,5] Comparing the results of the more general theory, we find that under certain conditions, in which we get strong

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