Mesogen-jacketed liquid crystalline polymers via stable free radical polymerization

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SUMMARY: Stable free radical polymerization has been used in the controlled synthesis of poly(2,5-bis[(4-butylbenzoyl)oxy]styrene), PBBOS. This "mesogen-jacketed liquid crystalline polymer", which has mesogenic units attached directly to the backbone in a side-on mode, has been found to exhibit thermotropic liquid crystallinity similar to more conventional main-chain architectures. Stable free radical polymerization of PBBOS consistently produced molecular weight distributions below the theoretical limiting polydispersity of 1.5 calculated for a conventional free radical polymerization process. Surprisingly, a comparison of the synthesis of polystyrene to the polymerization of PBBOS under nearly identical conditions showed that the PBBOS polymerized with a significantly higher reaction rate and monomer conversion efficiency. The nematic phase of these polymers was determined to be stable over the temperature range spanning the polymer glass transition temperature up to the temperature for thermal decomposition. The molecular arrangement of the PBBOS polymers was examined by wide-angle X-ray diffraction and is described here.

Introduction

Stable (or controlled) free radical polymerization (SFRP)[a] has gained in importance over the last few years because it can be applied to the controlled radical synthesis of both block copolymers and homopolymers. Based on initiating systems of either 2,2,6,6-tetramethyl-piperidinyl-1-oxy (TEMPO) and benzoyl peroxide (BPO) or an initiator such as 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-ethane (**1**) (see Fig. 1), the SFRP process has been demonstrated to work extremely well for styrene and its derivatives[1–5]. As an example of the diversity of materials so far produced, star polymers have been prepared using multisite initiators. Unusual monomers such as vinylbenzyl chloride have been polymerized with little branching.

Other variations of controlled radical polymerization using activated halogens have now been developed that
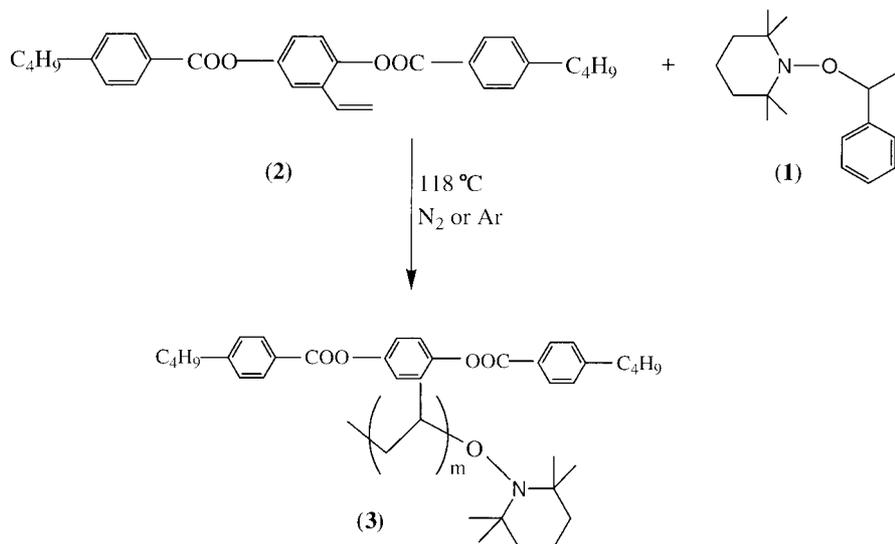

Fig. 1.   Scheme of synthesis of poly(2,5-bis[(4-butylbenzoyl)-oxy]styrene) (PBBOS) via stable free radical polymerization

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[a]   Stable free radical polymerization, living free radical polymerization and controlled radical polymerization are terms for radical polymerization in the presence of a radical trapping species.
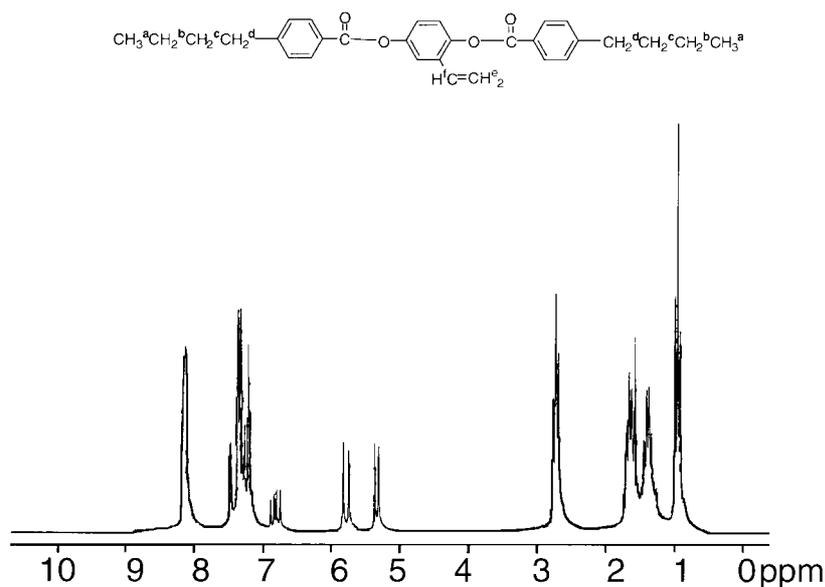
Fig. 2. ¹H NMR spectrum of 2,5-bis[(4-butylbenzoyl)oxy]styrene (BBOS) at room temperature in CDCl₃

successfully produce narrow molecular weight distribution methacrylates[6–8]. Examples of side group LC poly-(methacrylates) formed by atom transfer radical polymerization have also been prepared and studied by Pugh et al.[8] The SFRP procedure has been successfully applied to styrene-based monomers for the synthesis of side group liquid crystalline polymers with the mesogenic units longitudinally attached to the flexible main chain[9]. In these materials, the side group was attached to a vinyl phenol group, a monomer that had been previously polymerized by SFRP in other structures.

In this paper, we report the synthesis via SFRP of the mesogen jacketed liquid crystalline polymer, poly(2,5-[(4-butylbenzoyl)oxy]styrene), PBBOS (**3**), using (**1**) as initiator. PBBOS has been previously synthesized via conventional radical polymerization by Zhou et al.[10] The monomer is interesting because it is based on vinylhydroquinone, a monomer that has been largely unexplored in recent times. The resulting polymer has been reported to be a side group LC polymer with mesogenic units attached directly to the backbone in a side-on mode to form a "mesogen-jacketed liquid crystalline polymer" (MJLCP)[11, 12]. For this class of polymers, the presence of a flexible spacer between the backbone and the mesogenic units is unnecessary for mesophase formation, in contrast to the need for such a spacer in conventional (end-attached) side group LCPs[13]. The steric crowding between the backbone and the rigid and bulky mesogenic units acts to stiffen the chain backbone, leading to polymers that behave as semi-rigid *main chain* liquid crystalline polymers (MCLCPs) with persistence lengths in the range of 15 nm[14, 15]. Consequently, MJLCPs are distinct

from both conventional main chain and side group LC polymers and form a unique class of main chain LC polymers that can be synthesized by conventional chain polymerization (e.g., radical polymerization). The use of controlled radical polymerization to synthesize a MJLCP, such as PBBOS, permits the synthesis of new polymers with low polydispersity, and potentially rod-coil block copolymers. In this paper, we present the SFRP synthesis of a mesogen jacketed LC polymer, PBBOS, along with a description of some of its physical properties.

Experimental part

Synthesis

The monomer, 2,5-bis[(4-butylbenzoyl)oxy]styrene, BBOS, ((**2**), Fig. 1), was synthesized by reaction of 2-vinyl-1,4-dihydroxybenzene and 4-butylbenzoyl chloride according to the method described by Zhou et al.[10]

¹H NMR (CDCl₃): δ = 0.95 ppm, 6H for CH$_3^a$, 1.35 ppm, 4H for CH$_2^b$, 1.65 ppm, 4H for CH$_2^c$, 2.70 ppm, 4H for CH$_2^d$, 5.10–5.90 ppm, 2H for = CH$_2^e$, 6.60–6.95 ppm, 1H for —CH^f = and 7.00–8.30 ppm, 11H for the phenylene rings (Fig. 2).

BBOS possesses a smectic phase (Fig. 3) between its melting point (60 °C) and its clearing temperature (95 °C) (see DSC thermogram in Fig. 4). The higher melting point obtained for this compound, compared with the literature values presented in ref.[10], is likely attributable to its higher purity.

The polymerizations were carried out in bulk, first heating the monomer, 2,5-bis[(4-butylbenzoyl)oxy]styrene (**2**), and initiator (**1**) (purchased from Binrad, Inc.) in a molar ratio of 100/0.3 at 80 °C under inert atmosphere for 5 min and then
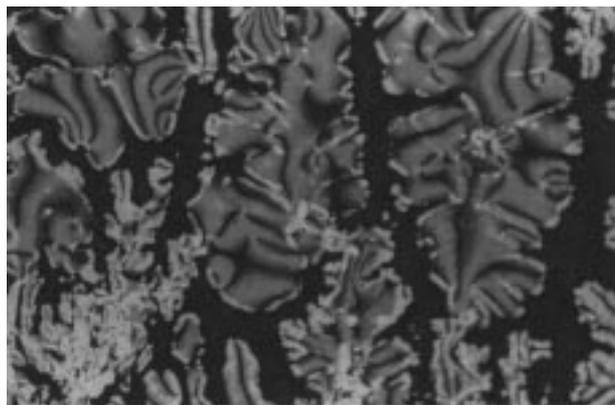
Fig. 3.   A photomicrograph of 2,5-bis[(4-butylbenzoyl)oxy]-styrene (BBOS) taken at 84 °C showing a smectic mesophase
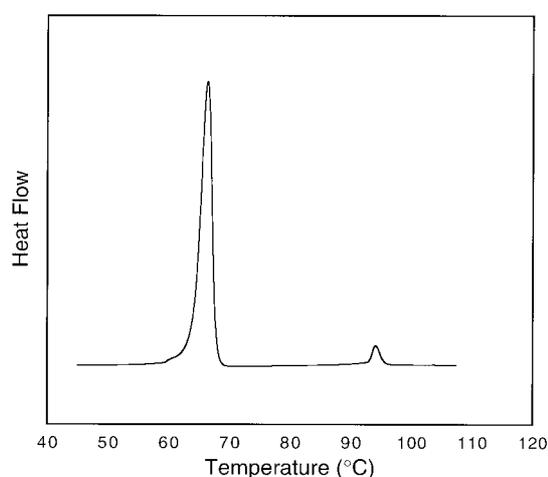

Fig. 4.   DSC curve of 2,5-bis[(4-butylbenzoyl)oxy]styrene (BBOS) (N$_2$, 10 °C/min)

heating the mixture to 118 °C. Reaction times between 0.5 and 20 h were used. PBBOS (3) was precipitated in methanol and dried in a vacuum oven at room temperature.

Characterization

A Varian XL 200 MHz NMR was used with chloroform-*d* as solvent to obtain NMR spectra of all the compounds. Thermal analysis was carried out under a nitrogen atmosphere by means of Perkin Elmer DSC7 and TGA7 instruments using a heating rate of 10 °C/min. The liquid crystalline properties of all compounds were characterized using a Nikon HFX-DX polarizing microscope with a Mettler FP80 heating stage. Measurement of molecular weight and polydispersity of all polymer samples were carried out by gel permeation chromatography (GPC) equipped using four Waters Ultrastyragel HT columns (connected in series) operating at 31 °C. THF was used as the solvent and the GPC was operated at 0.3 ml/min. Solution concentrations of 1.0 mg/mL and solution volumes of 20 µL were employed. GPC data were collected using a Waters 490 programmable multiwavelength detector, and molecular weights were calculated from GPC elution volume data using monodisperse polystyrene standards.

Wide-angle X-ray scattering (WAXS) experiments were conducted with a Rigaku rotating anode X-ray generator operated at 40 kV and 260 mA, using a copper target and a graphite monochromator. A parallel bundle of about 5–10 fibers drawn from the nematic melt was placed on a pinhole collimator in a vertical orientation, and the diffraction patterns were recorded on a phosphoric image plate using a Statton camera at room temperature. Diffraction patterns were obtained by scanning the phosphoric image plate using a Molecular Dynamics Storm 820 image-plate reader. The diffraction peak positions (*d*-spacings) and widths were calibrated with silicon powder, and the intensities were corrected for absorption, polarization, and scattering geometry factors. Intensity profiles as a function of the Bragg angle (2θ) were obtained using ImageTool software. UTHSCSA ImageTool is beta-version software available by anonymous FTP from maxrad6.uthscsa.edu.

Results and discussion

Synthesis

The monomer, 2,5-bis[(4-butylbenzoyl)oxy]styrene, BBOS, has been shown to form semi-rigid LC polymers by radical polymerization. We observed that BBOS is a very reactive monomer when polymerized under stable free radical conditions that use **1** as initiator. Tab. 1 shows the molecular weight, polydispersity, and monomer conversion data for different samples of PBBOS obtained using different reaction times under bulk polymerization conditions. Molecular weights were determined by gel permeation chromatography on samples taken directly from the reaction mixture and are reported as polystyrene equivalent molecular weights. Polydispersity values were calculated as the ratio of $\overline{M}_w$ to $\overline{M}_n$. Conversions were obtained by comparing the relative areas for the monomer and polymer UV peaks on each chromatogram. As expected for SFR polymerization conditions, each sample of PBBOS had a narrow molecular weight distribution (Fig. 5). In every case, it was always below the theoretical limiting polydispersity of 1.5 calculated for a conventional free radical process[19]. In contrast, only extremely polydisperse samples PBBOS (PDI $\approx$ 3) were obtained by Zhou et al. by conventional free radical polymerization using AIBN as initiator. Moreover, we were readily

Tab. 1.   Polymerization of PBBOS (molar ratio monomer (BBOS)/initiator: 1000/3)

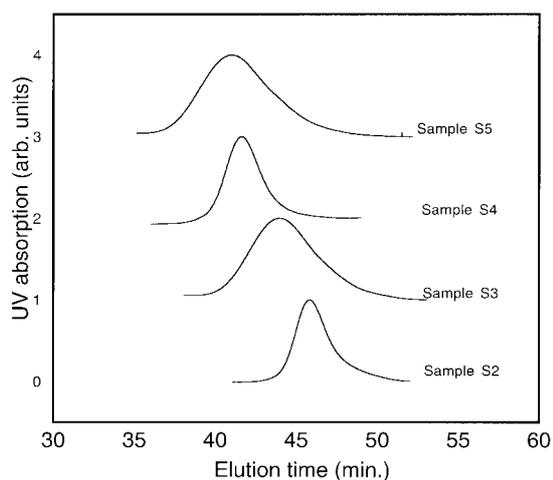| Sample	$\overline{M}_n$	$\overline{M}_w$	PDI	Time in h	Conv. in %	$\ln M_0/M_t$
S1	4 800	6 770	1.41	0.5	17	0.19
S2	18 600	23 600	1.27	2.5	34	0.42
S3	31 200	40 500	1.30	4	48	0.65
S4	48 000	61 000	1.27	15	60	0.65
S5	51 000	66 000	1.29	20	67	1.10

Fig. 5. GPC curves of poly(2,5-bis[(4-butylbenzoyl)oxy]styrene) (PBBOS) samples (see Tab. 1) showing the incremental increase of molecular weight with time
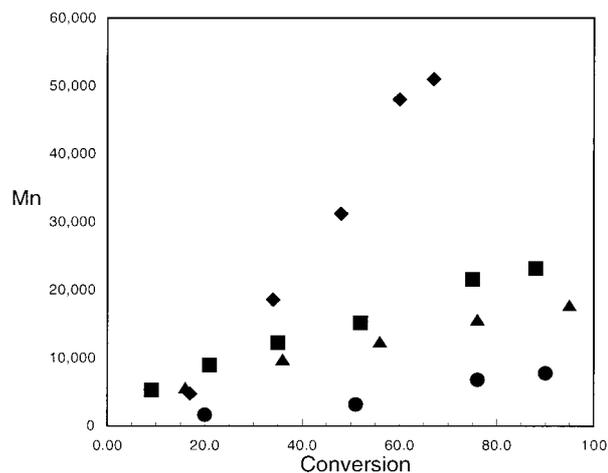

Fig. 6. Plot of $\overline{M}_n$ (●) and %-conversion (■) for poly(2,5-bis[(4-butylbenzoyl)oxy]styrene) (PBBOS) versus time of reaction (see also Tab. 1)

Fig. 7. Plot of $\overline{M}_n$ versus conversion in a comparison between polystyrene (PS) and poly(2,5-bis[(4-butylbenzoyl)oxy]styrene) (PBBOS) synthesized via SFRP under nearly identical conditions. (◆) PBBOS, (●) PS (synthesized at 123 °C, no additives. See also ref.[1]), (■) PS (synthesized at 130 °C and using camphorsulfonic acid (CSA) as additive. See also ref.[20]), (▲) PS (synthesized at 125 °C and using FMPTS as additive. See also ref.[21])
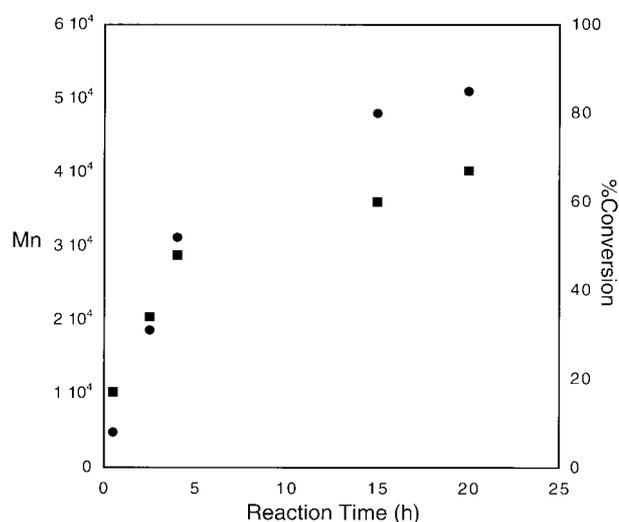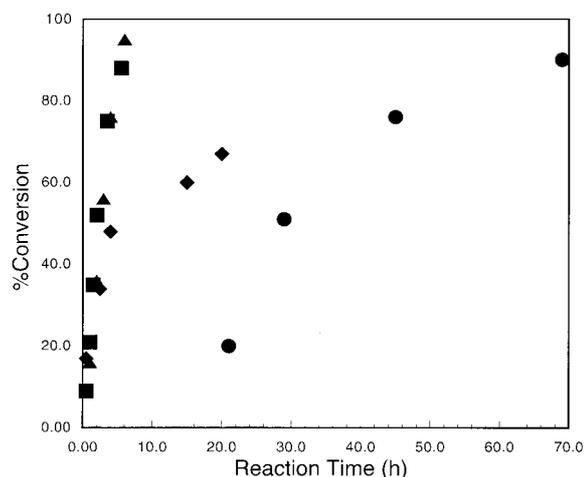

Fig. 8. Percent conversion versus time of reaction, a comparison between polystyrene (PS) and poly(2,5-bis[(4-butylbenzoyl)oxy]styrene) (PBBOS) synthesized via SFRP under nearly identical conditions. (◆) PBBOS, (●) PS (synthesized at 123 °C, no additives. See also ref.[1]), (■) PS (synthesized at 130 °C and using CSA as additive. See also ref.[20]), (▲) PS (synthesized at 125 °C and using FMPTS as additive. See also ref.[21])

able to control both the resulting molecular weight of each PBBOS sample and monomer conversion by length of reaction time (Fig. 6).

As typical of SFRP reactions, it was observed that the molecular weight of the growing polymer chain gradually increased with time while maintaining its narrow molecular weight distribution (Fig. 7). The rate of polymerization was quite fast during the initial 4 h of reaction when 50% conversion of monomer is reached. In the subsequent reaction period, the molecular weight of the polymer continues to gradually increase, and after 20 h, molecular weights of ≈50 000 Dalton and a conversion equal to ≈70% can be obtained. These results are quite unusual if compared to those obtained for polystyrene synthesized via SFRP under nearly identical conditions. High molecular weight polystyrene ($\overline{M}_n$ >10 000 Dalton) can be

obtained at similar rates in high yield by SFRP only if particular additives, which help to increase the rate of polymerization, are present in the reaction mixture[20-23].

It was observed that this approach was unnecessary for formation of PBBOS. High molecular weights and conversions can be reached during the first hours of reaction without any additives and at lower temperature than required for simple styrene polymerization. These high rates of polymerization occur at temperatures at least 15 °C lower than usually reported for PS (see Fig. 7 and 8). Moreover, it was observed that very high molecular

Tab. 2. Polymerization of PBBOS (molar ratio monomer (BBOS)/initiator: 1000/1)

Sample	$\overline{M}_n$	$\overline{M}_w$	PDI
S6	107 000	113 000	1.06
S7	108 000	122 000	1.13

weights of PBBOS, greater than 100 000 Dalton, and polydispersities less than 1.2 can be realized by decreasing the quantity of initiator in the mixture of reaction. Tab. 2 shows the polystyrene equivalent molecular weights and polydispersity results obtained for samples of PBBOS [S6 and S7] synthesized under the same conditions described above (conversion ≈20%), but using a molar ratio between monomer and initiator of 1000/1.

These results demonstrate several unusual features of this monomer and the important differences in the reaction state of BBOS compared to styrene. In searching for explanations of this higher rate of reactivity, it was noted that liquid crystallinity might play a role. Polymerizations were carried out at temperatures above those of the initial LC state of the monomer, but polymerization quickly induced formation of a new polymeric mesophase. This preordering may enable more efficient polymerization, as the monomers would be lined up. Preordering effects have been observed in many LC systems including some of those reported recently by Percec et al.[25] Since the monomer side groups lie roughly orthogonal to the polymer chain direction, backbone growth occurs perpendicular to the mesogenic group director. It is also possible that the electron withdrawing character of the benzoate groups on the monomer provide a more reactive state for SFRP. The effect of severe steric hindrance on the TEMPO is presently unknown. The eventual slowing down of the polymerization rate is probably due to the increased viscosity of these semirigid rod polymers.

We expect that BBOS is a very reactive monomer for block copolymerization. Preliminary results appear to confirm this view. Presently, we are exploring the possibility of synthesizing block copolymers of poly(acetoxystyrene-b-2,5-bis[(4-butylbenzoyl)oxy]styrene), starting from TEMPO-terminated poly(acetoxystyrene). We have observed that p-acetoxystyrene is a monomer with reactivity faster than styrene. A recent report by Zhou et al. describes the preparation of block copolymers based on styrene with a BBOS-like monomer[26].

Thermal characterization

Initial characterization has revealed that all the samples of PBBOS were not crystalline, but instead are glassy, mesophase-forming polymers with a glass transition temperature ≈30 °C. Above this temperature, PBBOS becomes birefringent and a nematic mesophase can be
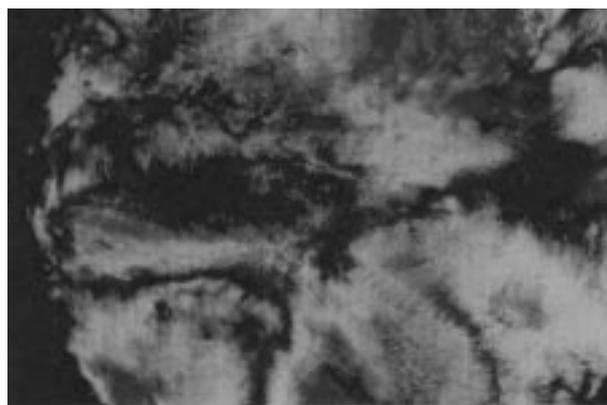

Fig. 9. Photomicrograph of poly(2,5-bis[(4-butylbenzoyl)oxy]styrene) (PBBOS) taken at 148 °C showing a nematic mesophase

observed (Fig. 9). It was impossible to observe any clearing transition, because the polymer decomposes before reaching its nematic-isotropic transition temperature ("clearing point"). Additionally, a 10% weight loss was observed at 380 °C by TGA. These thermal data are consistent with the data previously published by Zhou et al.[10]

X-ray data analysis

The X-ray diffraction patterns obtained for fibers of PBBOS, S8 ($\overline{M}_n$ = 87 K) and S9 ($\overline{M}_n$ = 39 K) drawn from the nematic melt are shown in Fig. 10 in which the fiber axis is vertical. Two characteristic reflections appear in the patterns, one being a strong, oriented arc on the equator, and the second being a diffuse and lightly oriented diffraction signal on the meridian. Previously, Xu et al.[16] reported similar X-ray results on their shear-oriented samples. The relatively sharp diffraction attributed to the distance between polymer backbones is highly intense around the equator, indicating that the chains are preferentially oriented along the draw direction. The outer diffraction peak, attributed to the spatial correlation between mesogenic units, is weakly concentrated around the meridian, indicating that the axes of mesogens tend to orient perpendicular to the polymer chains. The orientational order parameters ($\langle P_2 \rangle$) have been determined[17,18] and compared between S8 (Fig. 10a) and S9 (Fig. 10b) by scanning azimuthally both the inner and outer diffraction rings. The inner diffraction peak for S8 yields $\langle P_2 \rangle$ = 0.50 ±0.02, while the same peak for S9 (lower MW) yields $\langle P_2 \rangle$ = 0.49 ± 0.02, indicating no significant effect of molecular weight. In contrast, the orientational order parameters measured from the outer diffraction peaks are of much lower value, indicating that the mesogens are relatively less oriented. In particular, we have found that for the outer diffraction peak $\langle P_2 \rangle$ = 0.34 ±0.02 for S8, while $\langle P_2 \rangle$ = 0.31 ±0.02 for S9. In light of the lack of MW-dependence for the inner-peak $\langle P_2 \rangle$ data, this outer
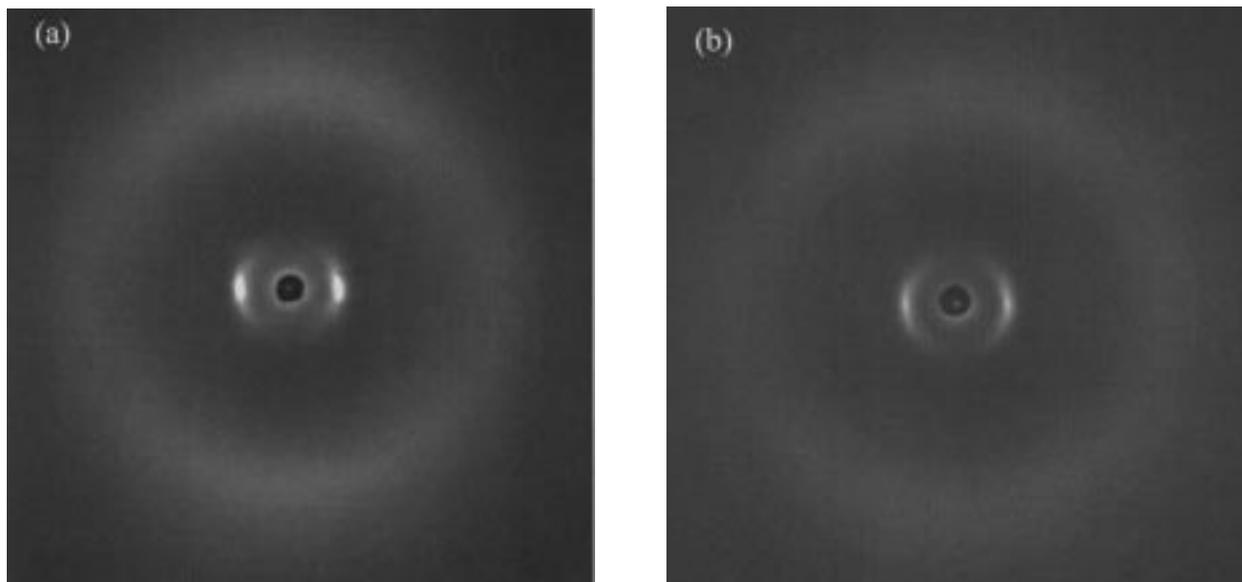
Fig. 10. X-ray diffraction patterns obtained from (a) high molecular weight polymer (S8) and (b) low molecular weight polymer (S9) by drawing a fiber from the nematic melt. The contrast of each pattern has been digitally enhanced for viewing purpose, while data analysis has been performed on unenhanced diffraction patterns. The fiber axis is vertical
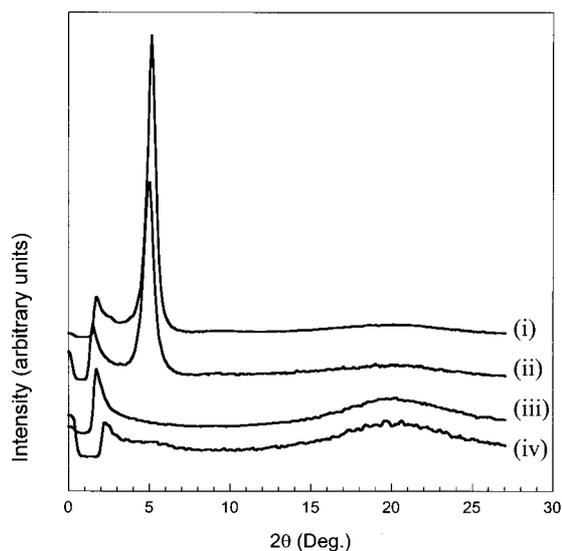

Fig. 11. WAXS profiles of high (i) and low (ii) molecular weight polymers along the equator and WAXS profiles of high (iii) and low (iv) molecular weight polymers along the meridian

and *iv* in Fig. 11) which represent the intermolecular distance between the mesogenic units show diffuse scattering at $2\theta = 19.8°$ ($d \approx 4.5$ Å), caused by the liquid-like association of the aligned mesogenic groups. Comparison of high and low molecular weight polymers reveals that the meridional intensity profiles are exactly coincident with each other as shown in Fig. 11. This interesting result suggests that the compactness of lateral packing of polymer backbones does not seriously affect the correlation length between mesogens, an observation consistent with $\langle P_2 \rangle$ measurements discussed above. Moreover, this observation suggests nematic biaxiality in PBBOS with some independence of backbone and mesogen directors. The ability provided by SFRP formation of these polymers to control molecular weight, molecular weight distribution and polymer chain architecture makes these materials useful models of main chain LC polymers for future investigations in polymer physics.

peak data indicates a degree of orientational independence for the mesogenic units with respect to the main chains.

Fig. 11 shows the plots of intensity versus 2θ for both high (S8) and low (S9) molecular weight polymers. The equatorial spacings (*i* and *ii*) provide information regarding interchain packing distance which is slightly decreased from ≈ 8 Å ($2\theta = 4.9°$) for sample S9 to ≈ 7.2 Å ($2\theta = 5.1°$) for sample S8, indicating a more ordered and compact structure developed in the high molecular weight polymer. The meridional spacings (*iii*

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