

Influence of molecular rigidity on interfacial ordering in diphenyl-based polysiloxane films

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Abstract

Synchrotron X-ray reflectivity (XRR) shows significant differences between the ordering in thin films of diphenyl-based siloxane oligomers with single versus double backbones of $-\text{Si}-\text{O}-$ repeating groups. We show that the more restricted conformational arrangement of twofold-skeleton molecules results in a higher degree of molecular ordering indicated by 2–2.5 times higher value of intensity of the corresponding Bragg peak in thin solid films of poly(phenylsilsesquioxane) than in films of poly(diphenylsiloxane), regardless of the solvent used for film casting. In both cases, the ordered molecules are located within 40–50 Å of the substrate surface. The results indicate unambiguously that the chain stiffness of siloxanes governs the degree of ordering in the restricted geometry of the interfacial region.

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1. Introduction

During the last decade there has been continued interest in developing a fundamental understanding of the structural and conformational behaviors of different molecules near a solid substrate. However, recent efforts to develop nanocomposite materials have given additional impetus for studies of polymers adsorbed on different surfaces and the resulting changes in their topologies. An understanding of polymer chain dynamics and equilibrium structure near surfaces and interfaces is very important for manufacturing functional layers in nanometer scale and for their use in coatings, adhesives, emulsions and devices.

The evolution and stabilization of ultrathin polymer films (~ 100 nm) are affected by effective molecular interactions, for example, long-range van der Waals and short-range electrostatic interactions and entropic factors [1]. Restricted geometries impose constraints on the possible molecular conformations. The interplay of surface-specific interactions, geometric factors

and the inherent flexibility/rigidity of molecules can lead to positional alignment (layering) of molecules at the interface and/or changes in their shapes, leading to extended, flat conformations. A key to understand polymer thin films is to delineate the impact of these factors on the equilibrium structure near the solid surface.

While thermodynamic interactions between polymers and substrate govern the equilibrium structure of polymer near the substrate surface, kinetic effects such as the evaporation rate of solvent, the solvent–polymer and solvent–substrate interactions, also play a critical role during the film formation process and in governing film morphologies. For example, in thin films cast from solutions containing rapidly evaporating solvents, fast evaporation rates create Marangoni instabilities, leading to high surface roughness [2]. Some recent studies attribute a crucial role to the solvent evaporation rate in the dynamics of film formation process. For example, authors in Ref. [3] claim that the structure of the films is dominated by the solvent evaporation rate. Further, they claim that since the polymer films from good and poor solvents did not exhibit any obvious difference, the interaction between the polymer chains and solvents is not an important factor in the dynamics of film formation process. A more complex description of the

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effect of solvent evaporation rates on the structure and morphology of thin polymer films is given in Ref. [4]. By the use of eight different solvents for deposition of polystyrene films on silicon substrate, the authors find that the resulting films are homogenous in the regime of low solvent vapor pressure, and the surface roughness is determined by the substrate. For intermediate solvent vapor pressures, distinct surface morphologies are detected, while smoother films are again obtained using solvents with high vapor pressure. These results pertain to the surface morphology of thin films of high molecular weight polymers obtained by a spin-coating process. In contrast, our previous studies [5–8] point to the critical role played by the competing interactions between the solvent, polymer molecules and the substrate in governing the resulting morphology of cast films of low molecular weight polymers. We found that when the interaction between the substrate and solvent is stronger than that between substrate and polymer, the films become rough and form segregated patches on the surface. When the substrate–polymer interaction is stronger than the solvent–substrate interaction, or when all interactions are weak, the resulting films are homogenous and flat. Because of these contradictory observations, the role of the solvent characteristics on the film formation process and in determining the structure of the polymer films must be investigated further.

Our studies of structural mesomorphism in thin liquid films of low molecular weight polymers (oligomers) [5–8] indicated that chain flexibility/rigidity plays a critical role in directing conformational arrangement near a solid substrate. However, all the observed structural phenomena were a result of many competing factors. In this work, we focus our attention to ordering in thin polymer films and its dependence on topological properties of molecular chains and solvent characteristics. To perform such studies, we chose two members of polysiloxane family with symmetrical side substituents on the silicon atom that have the potential to form ordered structures. These two oligomers have similar chemical structure and composition, except for with one essential difference: single- vs. double-chain structure of main siloxane backbone (Fig. 1).

Poly(diphenylsiloxane) (PDPS, Fig. 1a) is a polymer with liquid-crystalline properties, which can form a mesomorphic phase above its melting temperature [9]. Diffractograms show that PDPS macromolecules form ordered phases perpendicular to their axes with the interplanar distance of 9.9–10.4 Å [10–12]. The latest studies reveal that the preferred conformation for the siloxane backbone is a quasi-planar

structure consisting of alternating *cis*–*trans* sequential torsional angles along the polysiloxane chain [11]. Although the high molecular weight PDPS is only soluble in high-boiling-point solvents at temperature greater than 150 °C, the corresponding oligomers (with degrees of polymerization of less than 30) show significantly improved solubility in common organic solvents (toluene, chloroform, etc) [13]. It should be noted that the X-ray diffraction patterns for the mesomorphic phases of the oligomer and high molecular weight PDPS were found to be essentially the same [14].

Poly(phenylsilsesquioxane) (PPSQ, Fig. 1b) is a double-chained ladder-like polysiloxane with the formula $(\text{RSiO}_{3/2})_n$, where R is phenyl group [15]. PPSQ is readily soluble in common organic solvents (THF, chloroform, toluene, etc) and has numerous potential applications due to its film-forming ability, good thermal stability and mechanical properties [15–18]. X-ray diffractograms of PPSQ films show a relatively intense peak at 12.2–12.5 Å corresponding to the chain-to-chain distance that is characteristic of mesostructured materials. The average size of the ordered region varies between 18 and 47 Å as a function of the siloxane amount in the PPSQ samples.

To test the dependence of the surface morphology and structure of polymer films near the substrate on the specifics of the polymer–solvent system (nature of interactions between the polymer and the solvent, solution concentration, evaporation rate of solvent, etc) used for film deposition (see, for example, Refs. [2,3,19–22]), we used several common solvents.

2. Experimental

Silanol terminated poly(diphenylsiloxane and poly(phenylsilsesquioxane) samples were obtained from Gelest Inc. Co. (codes PDS-9931 and SST-3P01, respectively). The average molecular weights M_w of the samples were 1200 (PDPS) and 1400 (PPSQ), respectively. The substrates (3" × 1" × 0.1"), silicon (100) were purchased from Semiconductor Processing Inc. They were cleaned in a strong oxidizer, a mixture of 70% sulfuric acid and 30% hydrogen peroxide (70:30 v/v), for 45 min at 90 °C, rinsed with copious amount of pure water (18 MΩ cm), and stored under distilled water. Prior to preparing the films, the wafers were removed from the water and blown dry under a stream of nitrogen. We spread thin films by dipping the substrates in dilute solutions of PDPS and PPSQ in different solvents and withdrawing them at a constant speed of 1.5 mm/s. Solvents (HPLC grade) were purchased from Aldrich and used as received. The physical properties for the solvents used are shown in Table 1. Polymer solutions up to 5 wt% were prepared. No phase separation was observed with time. The films prepared by this method were dried in a vacuum oven at 40 °C for 12 h to remove any residual solvent.

X-ray reflectivity (XRR) studies were performed at the beam line X23B of the National Synchrotron Light Source, using a Huber four-circle diffractometer in the specular reflection mode (i.e., incident angle is equal to exit angle). X-rays of energy $E = 10$ keV ($\lambda = 1.24$ Å) were used for these measurements. The beam size was 0.40 mm vertically and

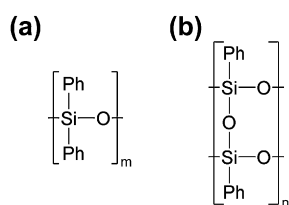


Fig. 1. Schematic diagram of the chemical structures of PDPS (a) and PPSQ (b) molecules.

Table 1
Characteristic data of solvents at room temperature [23,24]

Solvent	Formula	Molecular weight	ρ (g/cm ³)	ν_p (kPa)	ν	μ (D)	η (cP)	γ (mN/m)	δ_H
Acetone	C ₃ H ₆ O	58.09	0.784	30.8	5.6	2.69	0.303	22.68	19.7
Chloroform	CHCl ₃	119.38	1.480	26.3	11.6	1.04	0.542	26.67	18.9
THF	C ₄ H ₈ O	72.11	0.881	21.6	6.3	1.75	0.456	26.4	19.0
Benzene	C ₆ H ₆	78.11	0.874	12.69	5.1	0	0.603	28.2	18.8
Toluene	C ₇ H ₈	92.14	0.862	3.78	1.9	0.37	0.553	28.6	18.2
TCE	C ₂ H ₂ Cl ₄	167.85	1.586	0.813	0.65	1.32	1.575	35.58	20.2
DMTHF	C ₆ H ₁₂ O ₃	132.16	1.02	0.67		3.61*			

ρ – density (at 25 °C); ν_p – vapor pressure (at 25 °C); ν – relative evaporation rate (butyl acetate (BuAc) = 1); μ – electric dipole moment; η – viscosity; γ – surface tension; δ – Hildebrand solubility parameter; THF – tetrahydrofuran, TCE – 1,1,2,2-tetrachloroethane, DMTHF – 2,5-dimethoxytetrahydrofuran; * – MOPAC calculations.

1.0 mm horizontally. The resolution was $3 \times 10^{-3} \text{ \AA}^{-1}$. The samples were placed under helium during measurements to reduce background scattering and radiation damage. The experiments were performed at room temperature. The background was measured at $\theta \pm 0.1^\circ$ off to the specular direction and subtracted from the specular counts.

3. Results and discussion

We studied films of PDPS and PPSQ in the thickness range of 100–1000 Å. The influence of bulk characteristics on interfacial properties is the least for the thinnest films. Hence, the thinner the film the better suited it is for a comparative study of factors that influence the film morphology and structural ordering of molecules near a solid substrate. However, for the thinnest films (up to 250–300 Å) any manifestation of ordering in the specular reflectivity patterns was hindered by the observation of Kiessig fringes, which appear due to interference of reflected X-rays from film–air and film–substrate interfaces. For thicker films, increased surface roughness completely smears these fringes at high scattering angles. This allows for a clearer observation of evidence of molecular ordering in XRR data. Surface roughness of the films cast from different solvents was mainly determined by the Marangoni convection and did not show any regular dependence on the evaporation rate of the solvent. The surface topography behavior of PDPS and PPSQ films was quite similar: films were maximally flat in the case of tetrahydrofuran (THF), benzene or toluene, rougher for chloroform, and maximally rough when 1,1,2,2-tetrachloroethane (TCE) was used as solvent.

For thin films of thickness 250–1000 Å, a preferential orientation of PDPS and PPSQ molecules was detected in the film–substrate interface region by specular X-ray reflectivity. The typical reflectivity patterns for PDPS and PPSQ films of comparable thickness and cast from different solvents are shown in Fig. 2. The corresponding Bragg peak regions after background subtractions are shown in Fig. 3. The mean intermolecular spacing \bar{a} and the mean long-range dimension L (the characteristic size of the ordered regions), along the surface normal, were calculated from Ref. [25]:

$$\bar{a} = 2\pi/q_m; \quad L = \frac{\lambda}{\beta \cos\theta}, \quad (1)$$

where β is the full width at one half of the maximum intensity of the Bragg peak observed at a scattering angle of θ , and q_m is the reciprocal space coordinate of the Bragg peak.

These characteristics of the XRR patterns are independent of film thickness (for films in the thickness range 250–1000 Å). The obtained values of spacing, correlation length and ratio of integrated intensity of the reflectivity peaks for PPSQ and PDPS films deposited from different solvents are presented in Table 2. For both compounds, the position and breadth of the scattering peak indicates presence of a molecular

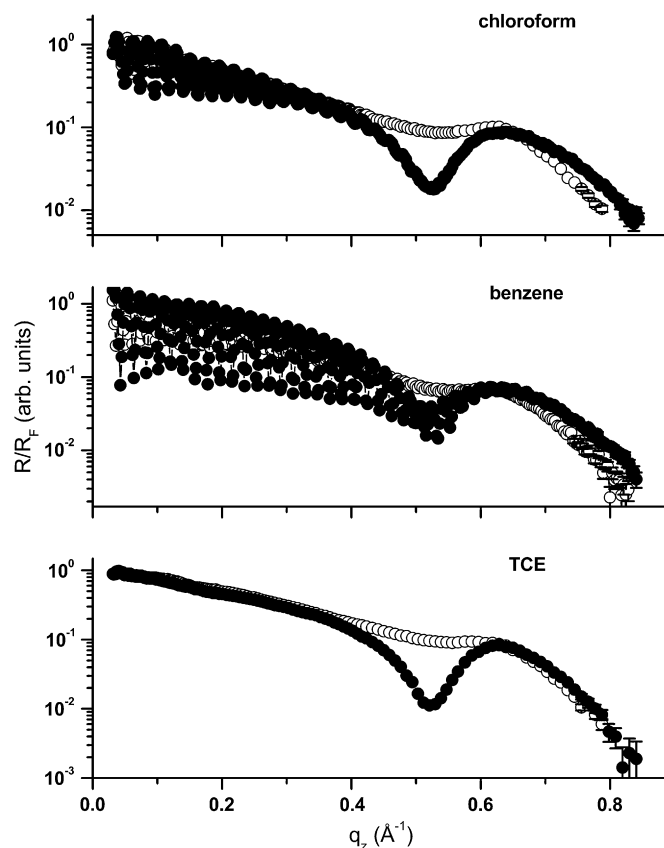


Fig. 2. Typical XRR data for thin films of PDPS (filled circles) and PPSQ (empty circles) deposited on the oxidized surface of silicon substrates from solutions in chloroform, benzene and TCE. Films thickness are: 392, 481, and 240 Å, respectively, for PDPS, and 285, 336, and 339 Å, respectively, for PPSQ (from top to bottom).

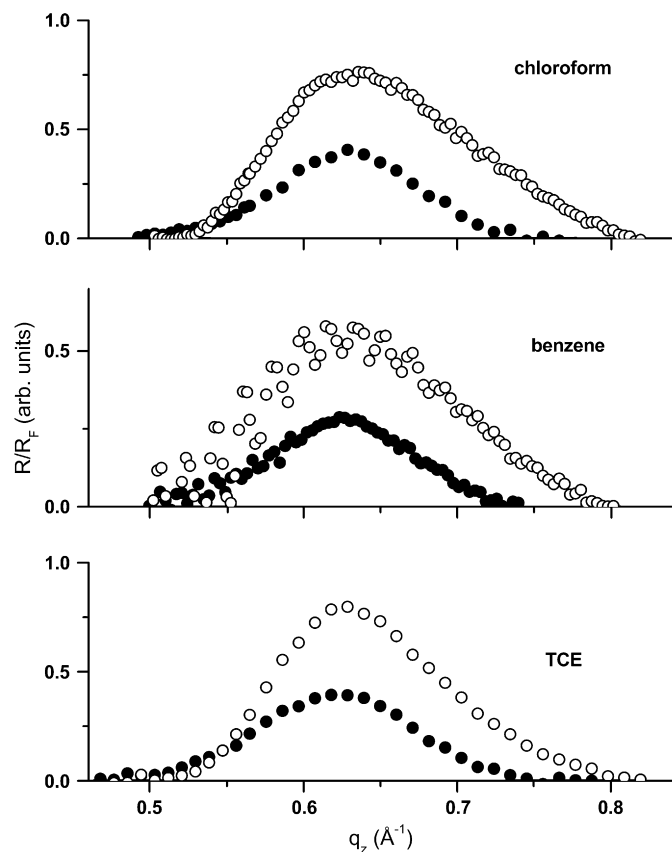


Fig. 3. Specular reflectivity of PDPS and PPSQ films in the region of the interference maximum after subtracting the reflectivity baselines.

ordering with a spacing of 9.9–10.2 Å and a correlation length of 40–60 Å. Irrespective of the solvent used for film preparation, PPSQ films show evidence of a more pronounced molecular alignment than PDPS. The intensity of the Bragg peak is at least 2–2.5 times higher for PPSQ films (Fig. 3). This intensity of the PDPS peak is practically invariant with film thickness. However, the ratio of peak intensities of PDPS and PPSQ peaks varies slightly with solvent type. The presence of a stable structural feature from all films indicates that the orientation order of molecular chains is an intrinsic feature of the surface layers.

The siloxane backbone has a large degree of flexibility in the presence of small side groups such as methyl or hydrogen. However, the backbone flexibility is diminished greatly when rigid and rather bulky phenyl groups are substituted on silicon. A measure of the polymer chain stiffness is the persistence length – the average distance traversed by the chain backbone

along its initial direction before the chain loses memory of this direction. This persistence length calculated for the PDPS sample under study is about 4.5 Å [26]. The value is twice the persistence length for PDMS (polydimethylsiloxane), the corresponding methyl substituted siloxane. This is due to the steric hindrance of the phenyl side groups, which hinders possible rotations about the single bonds of the main backbone of the polymeric chains. As a side note, it should be mentioned that the presence of oxygen atoms in the main backbone of the chains decreases the persistence length. For example, silane polymers (without alternating oxygen atoms in the main backbone) have almost twice the value of this parameter compared to siloxane polymers.

PPSQ has a significantly more rigid skeleton in which movement around the longitudinal axis is limited and conformation is less variable than for PDPS. The value of persistence length for ladder poly(phenylsiloxanes) varies from 40 to 100 Å (16–40 monomer units) [27]. This is in the range typical for ladder-like polysiloxanes of diverse structures. The high rigidity of such ladder polysiloxanes is a direct consequence of the double-chain structure of their molecular chains. Although the increased rigidity of PPSQ chains seems to be a sufficient factor for forming mesophase structures, the specific interaction of the side phenyl groups can undoubtedly favor this process. Phenyl groups preferentially orient perpendicular to their nearest neighbors. This tendency is a critical driving force for the orientation of the chains in the crystalline state.

Molecular simulations show that the chain-to-chain distance in PPSQ can vary from 8 Å (if PPSQ has *cis*-syndiotactic) to 11.8 Å (for *cis*-isotactic structure) [17]. Our XRR data give an average chain-to-chain distance of about 10.0–10.2 Å. It appears that the confined geometry conditions (reduced dimensionality near solid substrate) lead to conformation or/and spatial arrangement of molecules in this region, which are different from the bulk structures.

Irrespective of the solvent used for film preparation, the buried structure of polymer films near the substrate is quite similar. This can be seen from the Patterson functions presented in Fig. 4. The Patterson function is sensitive to the relative positions of the rapidly changing regions in the electron density distribution. The secondary peaks in 40–50 Å region are due to density oscillations in the films. The oscillations of $P(z)$ become “asymmetrical” with respect to the two interfaces for films of thickness over 200 Å (for thicker films they are absent close to the primary maximum, not shown in Fig. 4). This implies that the density fluctuations within the films studied are closer to the smoother interface, the substrate

Table 2
Spacing, correlation length and ratio of integrated intensity of the reflectivity peaks for PPSQ and PDPS films deposited from different solvents

Solvent	PPSQ		PDPS		$I_{\text{PPSQ}}/I_{\text{PDPS}}$
	\bar{a} (Å)	L (Å)	\bar{a} (Å)	L (Å)	
Chloroform	9.9–10.0	43–49	9.9–10.0	53–59	2.3
THF	9.9–10.0	46–53	9.9–10.2	52–59	1.5–1.7
Benzene	9.9–10.0	43–47	10.0–10.2	50–58	2.4–2.6
Toluene	9.9–10.0	42–48	10.0	50–59	2.2
TCE	9.9–10.0	49–53	10.1–10.3	53–58	2.1–2.3

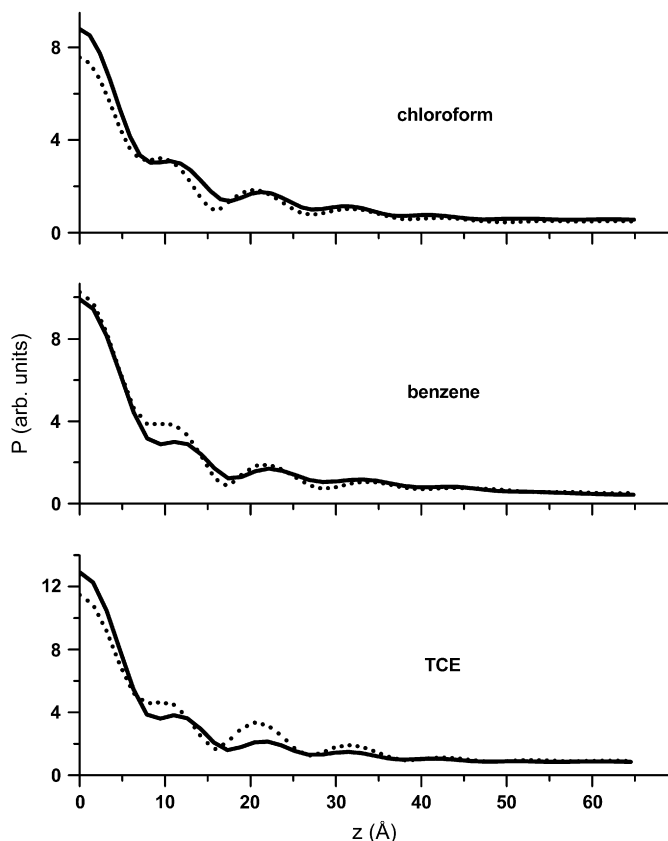


Fig. 4. Patterson functions from the observed XRR data presented in Fig. 2. Solid lines – PDPS films, dashed lines – PPSQ films.

[28]. The silicon substrate has a very low roughness ($\sim 3 \text{ \AA}$), but film roughness significantly increases for thicker films, as indicated by the smearing of Kiessig fringes (Fig. 2). As a result, ordering effects are located in the film–substrate interface region, not close to the film–air surface. This is a very common feature of various liquid/solid films under conditions of confinement near a solid surface and in the presence of weak interactions (but strong enough to establish and stabilize molecular order) between the film molecules and the substrate surface. In the case of PDPS and PPSQ films on silicon surfaces with native oxide layer, adhesion is enhanced due to attractive interactions between the phenyl polarizable groups and the OH groups of the substrate [8]. The value of 40–50 \AA is also a very common scale parameter for orientational ordering near solid substrate. Similar values were previously obtained for solid films of semi-rigid lyotropic hydroxypropylcellulose [29] and liquid films of flexible polydimethylsiloxanes [5,8].

The only distinct feature resulting from the use of different solvents lies in the reduction of the ratio of integrated peak intensities from PPSQ and PDPS when THF is the solvent (see Table 2). This difference results from the lower intensity of the ordering peak for PPSQ films. The peak amplitude for PDPS films is practically invariant with the type of solvent. To determine a possible origin of the observed feature, we analyzed the characteristic parameters of the solvents used (Table 2). Reduced ordering of PPSQ chains near the substrate can possibly

be explained by the effect of dipole–dipole interactions between THF and polymer molecules. It was reported recently that the surface roughness of polystyrene films depends upon the dipole moment of solvents [21]. However, no changes in the inner structure of the films were observed. Near-substrate film morphology was found to be a function of interaction strength between the polystyrene molecules and the substrate. In our case, in contrast, analysis of the relationship of solvent properties to ordering structure in our case indicates that the dipole moment of solvent is likely to be responsible for observed structural changes. THF is a rather polar aprotic solvent with electric dipole moment of 1.75 D. MOPAC calculations in Chem3D (CambridgeSoft) show that molecules of PPSQ have substantially higher dipole moment, 2.6 D, as compared with 1.6 D for PDPS. The stronger THF–PPSQ solute–solvent interactions may distort the inherent segmental motions of PPSQ molecules and lead to conformational rearrangements near the substrate. Since PPSQ molecules have a rigid skeleton in which movement (for example, around the longitudinal axis) is limited, such changes require a rather high dipole moment of solvent molecules.

To investigate further the important role of dipole moment of solvent on the ordering in diphenyl-based polysiloxane films, we prepared PPSQ films casted from solvents with a broad range of this parameter. Irrespective of the variations in other physico-chemical characteristics (for example, evaporation rate), the intensity of the reflectivity peak diminishes as dipole moment of the solvent increases (Fig. 5): maximum – for benzene (0 D), a lower intensity for THF (1.75 D) and a peak intensity of $\sim 50\%$ for DMTHF (3.61 D) and acetone (2.69 D). Slightly lower intensity value for acetone than that for DMTHF can be explained by extremely high difference in evaporation rates of these solvents. The trend is obvious:

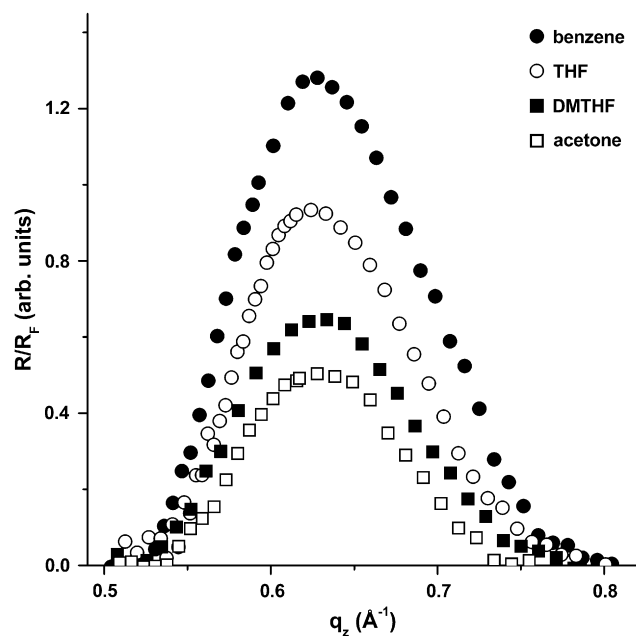


Fig. 5. Specular reflectivity of PPSQ films of thickness 700–900 \AA deposited from benzene, THF, DMTHF and acetone in the region of the interference maximum.

the role of solute–solvent interactions on the structure of solution-cast films cannot be underestimated and requires further systematic studies on different systems.

4. Conclusions

Our results indicate that for films cast from solvents with large variations in physical characteristics, such as evaporation rates, the structural changes near solid substrate are rather similar and mainly determined by the inherent properties of polymer chains in the restricted conditions of the interfacial region. The structure of the side groups in PDPS and PPSQ are similar, and the differences in degree of ordering appears to reflect the differences in conformational defects of molecular packing inside this confined sensitive region due to a ten-fold difference in the rigidity of double and single chain molecules. These conformational rearrangements are “frozen” during the film deposition process by the concomitant steric intermolecular interactions of the polymer chains.

We find that the film structure near the solid–liquid interface remains essentially similar. An intrinsic rigidity of these molecules together with stabilizing effect of π – π (aromatic–aromatic) interactions gives rise to an ordered phase near the substrate surface. The higher siloxane backbone flexibility in PDPS allows for a more efficient packing of the benzene rings in comparison to the more rigid twofold-based molecules of PPSQ, which show a higher degree of molecular ordering in the interfacial region. In both cases, the ordered region extends 40–50 Å from the substrate surface, and differences in ordering are due to defects of structural arrangements in this region. The chain ‘stiffness’ of siloxanes is responsible for such conformational changes in this restricted geometry during film deposition. Only rather strong (dipole–dipole) interactions between solute and solvent molecules can alter the packing of molecular chains at interface in the course of film formation.

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