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Molecular Orientation of Polyurethane Based Liquid Crystal Polymers by Corona Poling

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Molecular orientation induced by Corona poling of polyurethane based liquid crystalline polymers (LCPs) was studied using Fourier transform Infra-red with Grazing Incident Reflection Absorption Spectra (FTIR-GIRAS), Small-angle X-ray scattering (SAXS) and Atomic Force Microscopy (AFM). The FTIR-GIRAS spectra showed a reduction in peak intensity near 1729 cm⁻¹ due to bending of carbonyl group of urethane linkage. The P-E hysteresis curves showed higher remnant polarization (Pr) after poling. AFM showed numerous hills and valleys in the poled samples suggesting their use as piezoelectric materials. SAXS showed that the crystallinity of mesogenic monomer (cholesterol based) was reduced drastically in the polymers, however, the polymers with low a proportion (<16.7 mol%) of cholesterol possessed a residual crystallinity. LCPs are proposed to be suitable for piezoelectric applications (actuator, sensor etc).

Keywords: Molecular orientation, liquid crystalline polymer, corona poling, atomic force microscopy, Small-angle X-ray scattering, Piezoelectric materials.

1 Introduction

It is well known that polyurethanes show dipole moment due to the polar nature of their urethane linkage. Now, if an external electric field is applied, the uneven charge distribution in urethane segments could make a dipole alignment. It is also reported that Corona poling is an efficient process in which the charges from the corona discharge accumulate on the surface producing a high surface electric potential and align the molecules. In the polarization process, the dipoles are reoriented along the direction of the electric field (E). The alignment of the molecular chain is possible by applying a bipolar pulse which produces the P-E hysteresis loop. This loop is observed ideally from polyvinylidene fluoride (PVDF) and it is reported that the ferroelectric properties of PVDF are mainly due to the hysteresis effect of the dipole orientation (1). Similar alignment is also found for polymethylmethacrylate (PMMA) microdomain when applying a DC electric field (~40 kV/cm), for 24 h at an elevated temperature in an inert atmosphere (2). The molecular alignment, measured under synchrotron in real time conditions, is found to be suitable

for siloxane molecules while using an alternating electric field (3). The molecular alignment for a twisted nematic liquid crystal (LC) molecule using Fourier-transform infrared (FTIR) spectroscopy and Raman spectroscopy was also reported (4). The FTIR results suggest that the LC molecules undergo a restricted rotation about the molecular long axis. A normal mode associated with C–H out-of-plane wag on the LC core is found to be enhanced as the electric field is switched off. An electric field-induced smectic layer rearrangement has been reported in the smectic A phase of non-symmetric dimeric liquid crystals possessing cyanobiphenyl and phenylpyrimidine groups (5). The dimerization of mesogens likely lowers the stability of smectic layer structures, and smectic layers are rearranged by applying a low electric field in both planar and homeotropically aligned cell geometries. Electric-field-induced molecular reorientation is studied in the magnetically biased nematic LC film (6). Similar studies have been also done for flexible main-chain liquid-crystalline polymers (7–9) and side-chain liquid-crystalline polymers (e.g., side chain liquid crystal polyacetylenes, polypyrroles, and polythiophenes) (10–12). Surprisingly, there is no such report for the cholesteric liquid crystal polymers (ChLCPs) though these polymers may find important applications in the field of piezoelectric sensor, gas detector, paint industries, flat-panel displays, thermal imaging, nonlinear optical devices, rewritable full-color image recording, and photo-stable UV screens (13–16).

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In our present investigation we have synthesized a series of ChLCPs by a two-stage reaction of poly (ϵ -caprolactone diol) (PCL), 4,4'-methylene bis(phenyl isocyanate) (MDI), glycerol and cholesterol. In the first-stage, polyurethane backbone was made with PCL, MDI and glycerol and in the second-stage, mesogenic monomer cholesterol was added as a side chain via MDI. The electric field induced molecular alignment before and after poling of PU-based cholesteric liquid crystal polymers have been studied using FTIR-GIRAS, SAXS and AFM.

2 Experimental

2.1 Materials

PCL (MW = 3000) from the Solvay Co., U.K., 4,4'-methylene bis(phenyl isocyanate) (MDI) from Sigma-Aldrich, USA, glycerol from Shinyo Pure Chemicals, Japan, and cholesterol from Aldrich-Sigma, USA, were used for this study.

2.2 Synthesis of Liquid Crystal Polymers

The liquid crystal polymers were prepared in a two step process (Sch. 1); firstly, polyurethane block copolymer was synthesized from its monomers MDI, PCL, and glycerol in different mol ratio e.g., 4:3:1, 4:2:2 and 4:1:3 at 80°C for 90 min in a four-neck cylindrical vessel equipped with a mechanical stirrer under a nitrogen flow. Secondly, approximately 100 mL of dimethylformamide (DMF) was added to the neat PU, the temperature was maintained at 80°C, and required quantity of cholesterol with equimolar proportion of MDI, were added and the reaction was continued for another 30 min. The liquid crystal polymers were coded as L-1, L-2 and L-3, where cholesterol proportion varied from 10, 16.7 and 21.4 mol %, respectively (Table 1).

2.3 Characterization

For the $^1\text{H-NMR}$ characterizations, a Bruker Advanced DMX 500 spectrometer was used and the samples were prepared in CDCl_3 at room temperature. Corona poling was done under DC field of 15 kV at 1.5 cm gap using three-pin electrode for 20 min in open air. FTIR-GIRAS was performed using a Bruker IFS Electric (model: IFS 66V), with a resolution of 4 cm^{-1} for 1000 times scanning

in the range of $2000\text{--}500\text{ cm}^{-1}$. P-E hysteresis was done using a Ferroelectric Test System (model: P-LC100-X), a Precision Material Analyzer from Radiant Technologies Inc, NE, USA, with the applied voltage up to 20V. SAXS was studied using a Bruker AXS with General Area Detector Diffraction System (GADDS) using $\text{CuK}\alpha$ radiation in the angular range (2θ) of $0\text{--}9^\circ$ with a stepwise increase of $0.02^\circ/\text{min}$ and exposure time of 30 min. Surface morphology of the poled and unpoled samples was studied under an Atomic Force Microscope (model: XE 100) from Park Scientific Instruments Alliance (PSIA), CA, USA with non-contact mode at a scan rate of 1 Hz and scan area of $5\ \mu\text{m}$.

3 Results and Discussion

3.1 Formation of PU based LCP as confirmed by $^1\text{H-NMR}$ studies

Figure 1. shows $^1\text{H-NMR}$ spectrum of one PU based LCP (i.e., L-2 sample). The aliphatic protons of the glycerol in $\text{O-CH}_2\text{-CH(OH)-CH}_2\text{-O}$ appear at 4.09, 4.08, 4.09 ppm, respectively, whereas the protons of $\text{O-CH}_2\text{-CH}_2\text{-}$ coming from the PCL are observed at around 2.31 ppm to 2.32 ppm (17, 18). The presence of resonance peak at around 8.05 ppm is attributed to the aromatic protons from the MDI unit (17). The peaks at 2.92 and 2.97 ppm are for the protons coming from cyclic saturation of cholesterol, and peaks at around 1.69 to 2.31 for the aliphatic chain of cholesterol (19). Thus, $^1\text{H-NMR}$ confirms that cholesterol is added as a side chain to the backbone of polyurethane via an MDI molecule as described in Scheme 1.

3.2 SAXS Analysis of Unpoled Samples

Figure 2. shows SAXS diffractogram of cholesterol and different ChLCPs in the angular range of $0\text{--}9^\circ$ without poling. Cholesterol has two sharp peaks at $2\theta = 0.50^\circ$ and 2.60° (Figure 2(a)) giving the Bragg spacing in the range of $30\text{--}35\ \text{Å}$ which is equivalent to the molecular length of cholesterol as calculated from its most extended conformation (20).

Cholesterol has also two weak peaks at $2\theta = 5.25^\circ$ and 6.30° , this may be due to the presence of fused cyclic rings. The SAXS diffractograms of different cholesteric liquid crystal polymers are shown in Figure 2(b–d)). Here, we can see that the peaks at 5.25° and 6.30° of the cholesterol

Table 1. Compositions for PU based LCPs

Sample code	MDI (mol)	PCL (mol)	Glycerol (mol)	Cholesterol (mol)	Cholesterol (mol %)
L-1	4+1*	3	1	1	10.0
L-2	4+2*	2	2	2	16.7
L-3	4+3*	1	3	3	21.4

*mol of MDI added in the 2nd stage reaction.

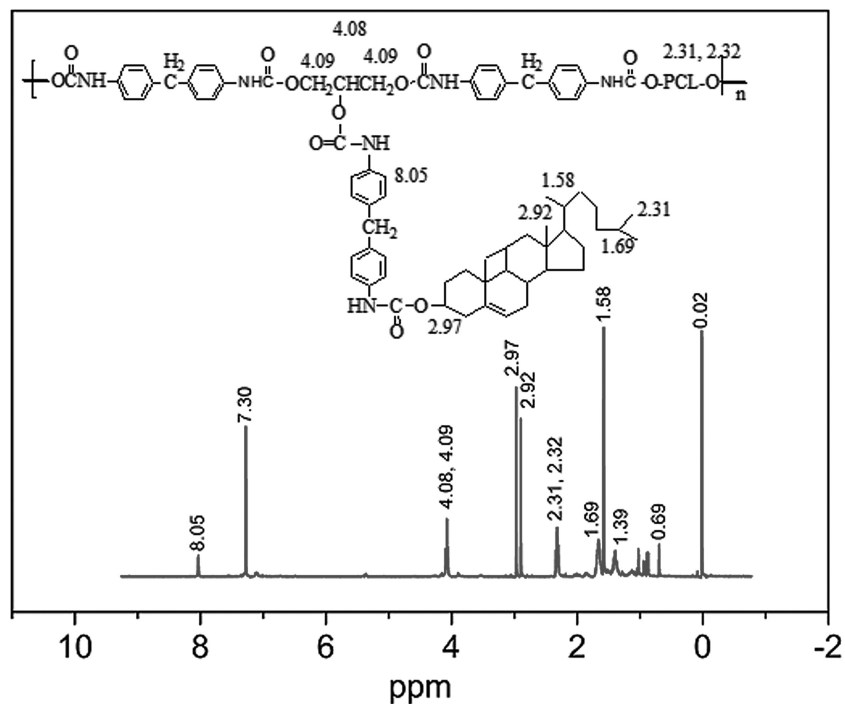
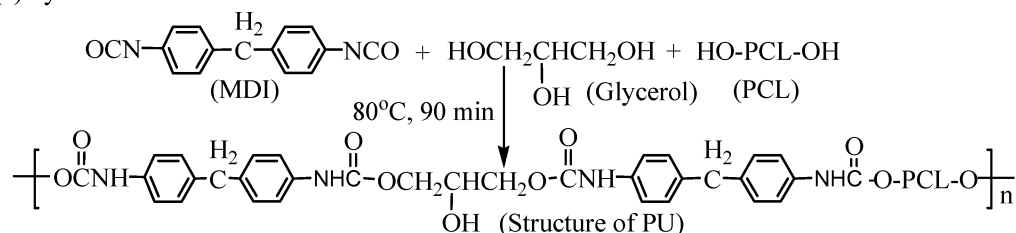


Fig. 1. Chemical shifts for PU based LCPs (i.e., L-2) and their assignments.

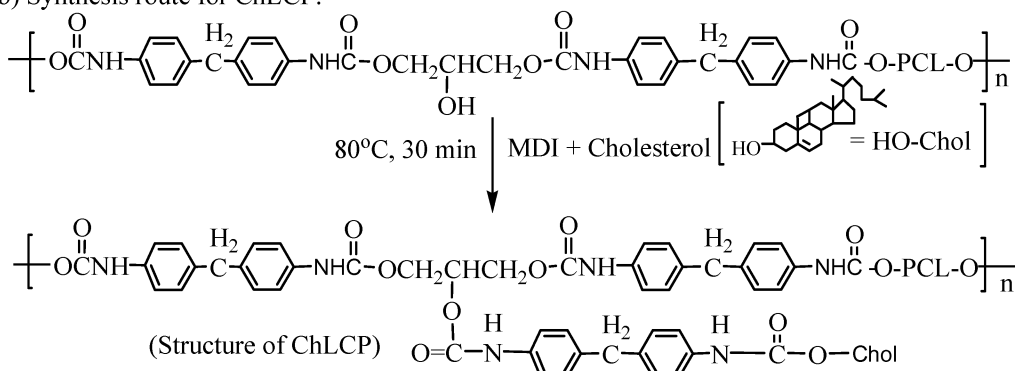
have been disappeared completely in the polymers. This may be due to difficult alignment of the rigid rings of the cholesterol in the polymers as the cholesterol molecules are pendant to the backbone PU chain at a specified distance. However, the polymers show a sharp peak near about $2\theta =$

$0.50 \sim 0.53^\circ$, corresponding to the alignment of short chain ethylene segments (21). The peak height at $2\theta = 2.60$ of neat cholesterol is reduced drastically in the polymers, though the lightly x-linked ChLCPs (e.g. L-1 and L-2) show to possess a residual peak intensity (Figure 2(b), (c)). It is

(a) Synthesis route for PU backbone:



(b) Synthesis route for ChLCP:



Sch. 1. Synthesis route for cholesteric liquid crystal polymers.

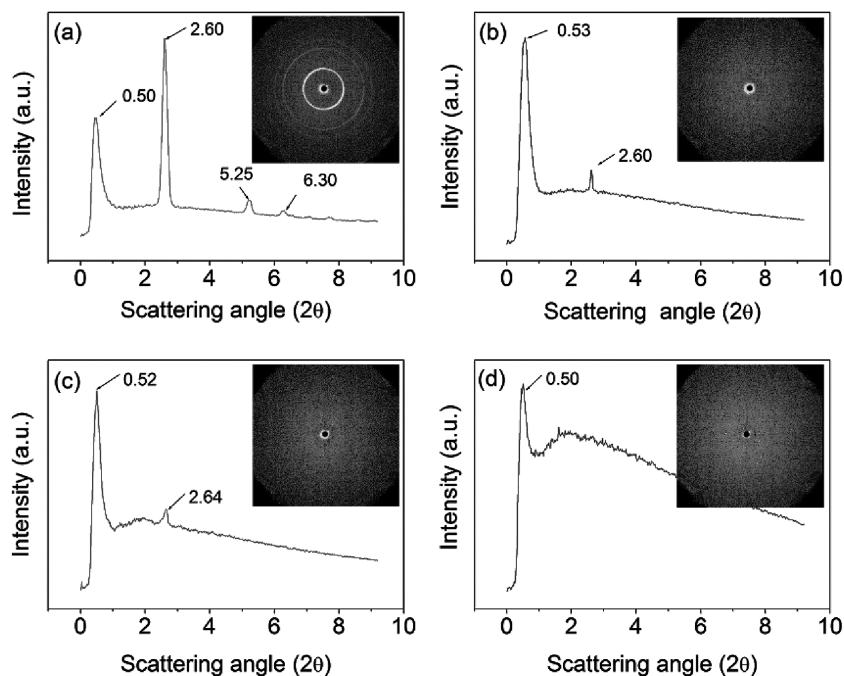


Fig. 2. Small-angle X-ray diffractograms of (a) cholesterol, (b) L-1 (c) L-2, and (d) L-3.

interesting to note that the peak near $2\theta = 2.60$ – 2.64 due to the presence of cholesterol disappears completely in L-3 (Fig 2(d)). This is because at higher cholesterol proportion the chance of x-link structure formation becomes high, which restricts the chain movement and their alignment to form a crystal zone (22). This implies that the cholesterol has been successfully incorporated into the PU chain.

3.3 P-E Hysteresis for Poled and Unpoled Samples

P-E hysteresis (Figure 3), measured under bipolar pulse of -20 V \sim $+20$ V for the samples before and after pooling, show that both the samples have similar polarization tendencies e.g., as the applied voltage increases the polarization also increases showing a large hysteresis loop under an external electrical field (23). However, the poled samples have more regular loops showing uniform polarization and

depolarization under the electrical field. It is also found that the poled samples have higher remnant polarization (Pr), the polarization at zero voltage during reversal of the external field, under same applied voltage compared to that of the unpoled one. For instance, the Pr values for poled and unpoled L-1 sample at 20 V are 0.5 and $1.2 \mu\text{C}/\text{cm}^2$, respectively (Figure 3(a)). The higher Pr value represents greater piezoelectric behavior of the polymers. Here the trend of the P-E hysteresis loops for all other ChLCPs are similar. But as the cholesterol proportion increases in the ChLCPs, the Pr value also increases implying that at higher cholesterol content depolarization is restricted due to the bulky cholesterol molecules. Thus during Corona poling molecular alignment is achieved by dipole orientation (24), caused by mainly bending of urethane carbonyl and ester carbonyl groups as confirmed from FTIR-GIRAS studies.

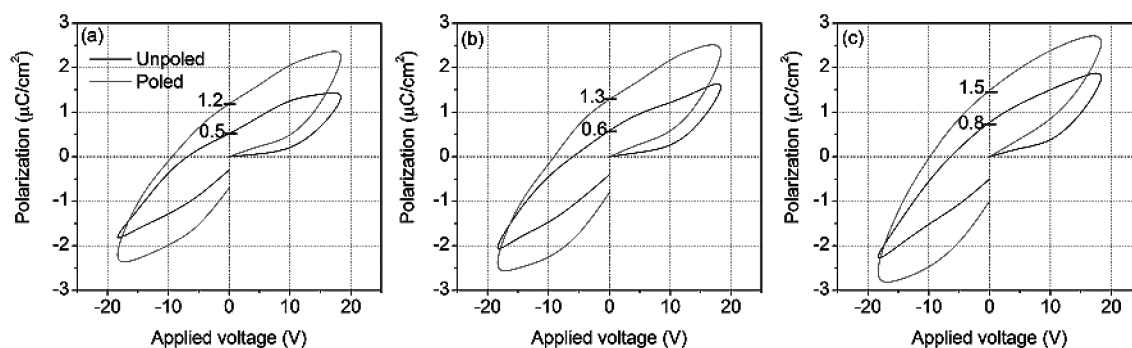


Fig. 3. P-E hysteresis measured by bipolar pulse of unpoled (black line) and poled samples (red line) of different ChLCPs, (a) L-1, (b) L-2 and (c) L-3.

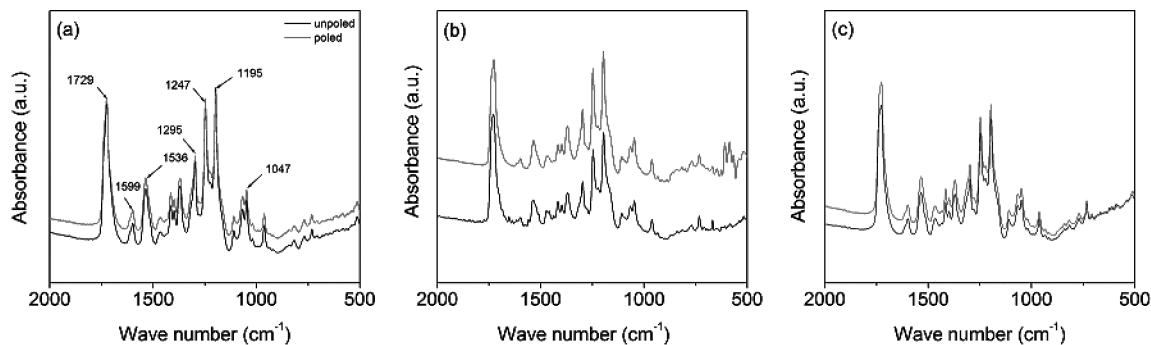


Fig. 4. FT-IR spectra of unpoled (black line) and poled samples (red line) of different ChLCPs, (a) L-1, (b) L-2 and (c) L-3.

3.4 Effect of Poling Studied by FTIR-GIRAS Spectra

Figure 4 shows the FTIR-GIRAS spectra of the different ChLCPs, before and after poling. Both the spectra show a very strong peak at 1729 cm^{-1} corresponding to the carbonyl group of the urethane linkage, peaks at 1599 , 1536 cm^{-1} for C-H scissoring and bending coming from glycerol and peaks at 1295 , 1247 and 1195 cm^{-1} for C-O stretching of the backbone chain (25). It is found that the absorbance at 1729 cm^{-1} before poling is 0.01786 and after poling is 0.01488 , thus the peak intensity at 1729 cm^{-1} is reduced by 16.68% (Figure 4(a)).

The reduction in peak intensity at 1195 cm^{-1} of this sample is also observed, whereas other peaks remain almost unchanged after poling. The reduction in peak intensity at

1729 cm^{-1} and 1195 cm^{-1} after poling clearly indicates the distortion of the carbonyl groups of the urethane and the ester linkages of the polyurethane backbone (26). There is no such extra peak due to the presence of cholesterol in the ChLCPs as all the specific absorptions are possible from the backbone PU chain. Again, it is reported that cholesterol has a spatial helicoidal structure and it contains a double bond in the second cyclohexane ring, and the two cyclohexane rings are not planar, consequently, it forms a layer structure as thin as 3 \AA (27). Thus, the double bond in cholesterol is under strain, which may form dipoles under electrical field. However, due to low proportion of cholesterol and insensitivity to FTIR, this double bond polarization is not detected clearly by FTIR spectroscopy.

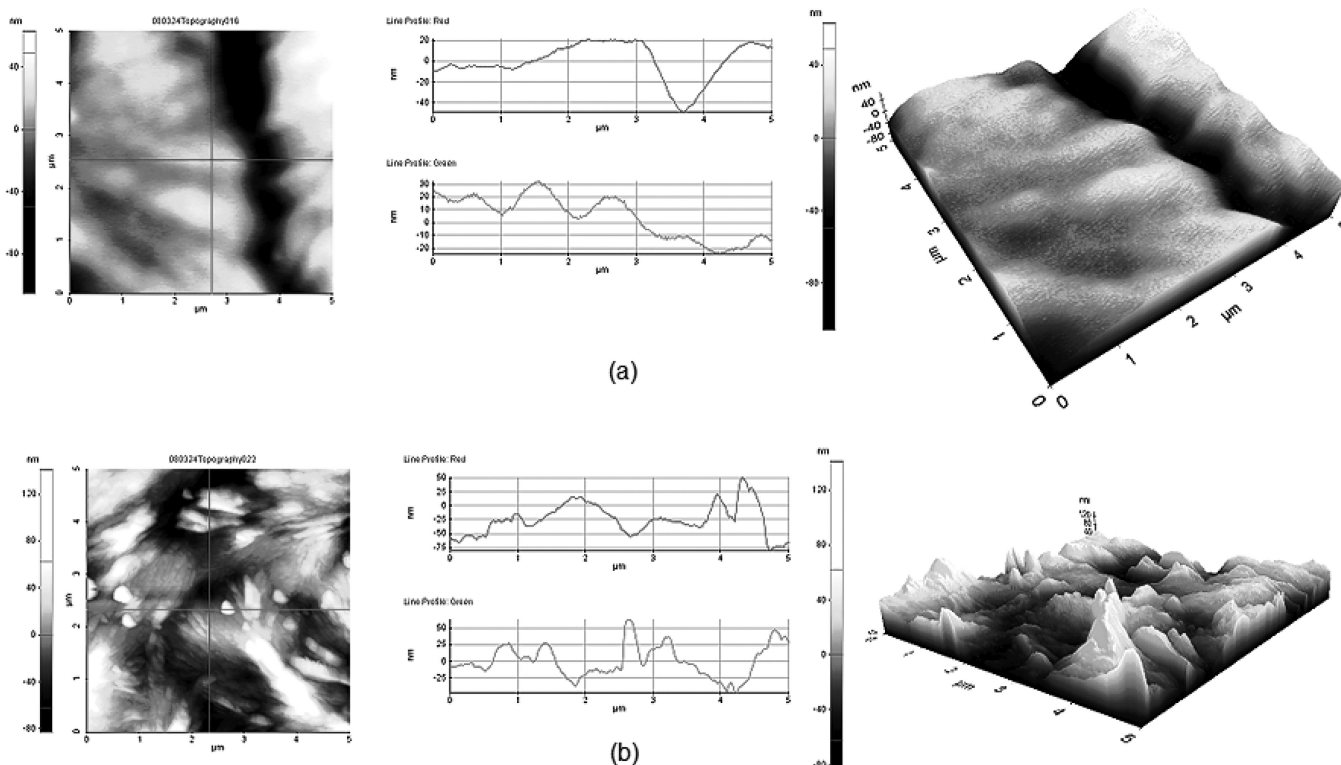


Fig. 5. AFM images of L-2 sample (a) before poling and (b) after poling.

3.5 Surface Morphology of Poled and Unpoled Samples

Figure 5. shows AFM scans of the spin-coated L-2 sample before and after Corona poling. The Fig. 5(a) is quite indicative that the surface of the film before poling is less rough compared to that after poling (Figure 5(b)) (24). In Figure 5(b), many parts have been protruded out from the surface after Corona poling, implying that urethane linkage of the cholesteric side chain has been interacted with the applied electrical voltage. Thus the polymer surface has been changed dramatically after poling, resulting in numerous hills and valleys in the surface structure, which were aligned to the poling direction (28, 29). During poling mainly side chain alignment is possible as its length is very small compared to that of the main chain and is free for movement (30). Moreover, it is also observed that the length of aligned molecular chain, measured from AFM micrographs increases as the proportion of cholesterol in the polymer increases (Figure not shown). For L-2 sample, the aligned molecular chain length is found to be approximately 30–35 nm which is high enough for its application as a piezoelectric material (31).

4 Conclusions

Electric field induced molecular alignment of polyurethane based side-chain ChLCPs, synthesized from PCL, MDI, glycerol and cholesterol by a two-step reaction, was studied using FTIR-GIRAS, SAXS and AFM. Spectroscopic analysis showed a decrease in peak intensity near 1729 cm^{-1} after Corona poling confirming bending and distortion of urethane carbonyl groups. As a result, there are numerous hills and valleys in the Corona poled samples. The poled samples showed higher remnant polarization (Pr) in the P-E hysteresis curves compared to their corresponding unpoled samples. SAXS showed that the crystallinity of neat cholesterol was reduced drastically in the ChLCPs as the free alignment of cholesteric part in the polymer was restricted due to x-linking between the polyurethane chains via MDI, however, the lightly x-linked ChLCPs showed a residual crystallinity. ChLCPs are proposed to be suitable for piezoelectric applications.

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