ChemComm

Domain formation in thin films of nonlinear optical side group polymers based on a rigid backbone

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Received (in Cambridge, UK) 17th August 1998, Accepted 12th October 1998

The NLO properties of a *N*-(4-nitrophenyl)-L-prolinol substituted poly(*p*-phenylene terephthalate) polymer are investigated.

Organic polymeric NLO materials are of great interest for practical applications such as electrooptic modulators and switches, due to their fast NLO response time, low cost, ease of fabrication, and large susceptibility. Extensive research efforts have been directed at tailoring organic molecules and their incorporation into polymeric matrices, and substantial progress has been made to reduce their relaxation and improve chromophore loading in the polymer matrix.[1–3] In our studies, we have focussed on rigid chain polymers such as poly(*p*-phenylene terephthalate)s with flexibly attached NLO substituents on the terephthalate moiety. For the pendant chromophore, *N*-(4-nitrophenyl)-L-prolinol was selected. These polymers did not exhibit thermotropic mesophases and the glass transition temperature (T_g) decreased significantly with increasing alkyl tether length, as expected.[4] The present paper deals with domain formation. Most of the results were obtained from the polyester with alkyl tether length of $n = 4$ (**P4**). The polymer was prepared *via* solution condensation of a chromophore-containing aromatic dicarboxylic acid chloride with hydroquinone in pyridine.[4] The number average molecular weight by gel permeation chromatography was 23,000 in $CHCl_3$ solution based on the polystyrene standard, and the polydispersity of molecular weight (M_w/M_n) was 7.1. The T_g of the polymer was about 68 °C. Polymer films were prepared by spin-coating polymer solutions in tetrachloroethane onto slide glass at 2000–4000 rpm and then treating the slides in a vacuum oven at 60 °C for over 24 h to remove the solvent. Second harmonic generation (SHG) was measured using a Q-switched Nd:YAG laser (1.064 μm) with a pulse repetition rate of 10 Hz. All AFM images were recorded with a Park Scientific Instruments Autoprobe LS, operated in a contact mode.

We studied the surface topographies of the spin coated films before and after corona poling using AFM. The poling was performed in a vertical wire 1 cm above the exposed polymer film. Fig. 1(*a*) shows an AFM scan of the spin coated film (thickness = 2.5 μm). The surface of the thin unpoled film is clean and extremely flat and the root mean squared (rms) roughness value was 2.4 Å. However, this excellent quality film was drastically changed after poling. Fig. 1(*b*) shows an AFM image of the poled film. Numerous mountain-like structures, aligned along the poling direction, were formed during poling. A similar surface morphology of larger size similar to microphase-separated block copolymers[5] was also observed in other samples by optical microscopy [Fig. 1(*c*)]. For the polymer with larger tether length, hills and valleys were also observed but the steepness and curvature decreased and the domains were not well developed compared to the polymer **P4**. As the length of the alkyl side chain increases, the polymer shows decreasing T_g values,[4] suggesting less prominent side chain coupling to the main chain; the growth of domains and their tendency to form would thus decrease. Although the surface topographies of the hills and valleys were characteristic of all the samples, their statistical data were different for each of the samples and preparation conditions studied. Despite the great variations in domain size, the investigated statistical data could be taken as a qualitative indicator of domain size when comparing experimental trends for the samples and poling conditions specified. Fig. 2 shows the growth of domains as a function of poling time obtained from the controlled experiments involving growth after quenching at successive poling times. A high degree of domain growth was achieved at relatively short poling times, and the height of the domains increased only moderately upon further poling. This growth pattern is similar to the two-mode growth in the measured SHG signals, which reached their stable levels after an initial rapid growth. From our data, no apparent differences were observed in the poling dynamics between these domain forming polymers and conventional side group polymers. However, the voltage applied in this study was limited to a relatively low voltage of 6 kV by the onset of film whitening. This whitening or clouding of the film was not associated with chemical degradation of the sample since the spectroscopic analysis did not indicated

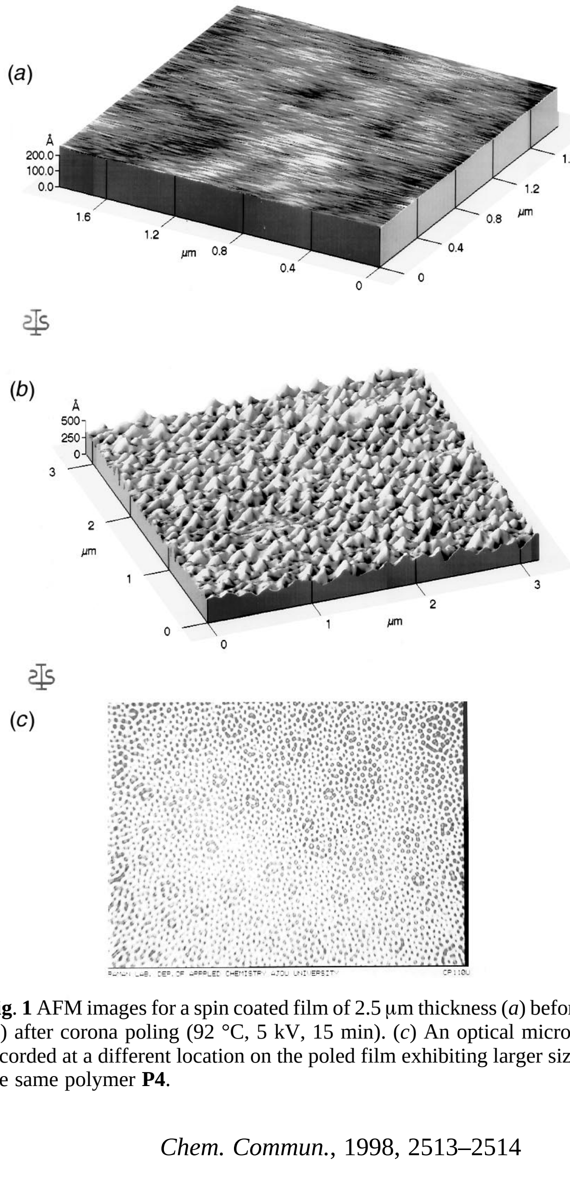

Fig. 1 AFM images for a spin coated film of 2.5 μm thickness (*a*) before and (*b*) after corona poling (92 °C, 5 kV, 15 min). (*c*) An optical micrograph recorded at a different location on the poled film exhibiting larger sizes for the same polymer **P4**.

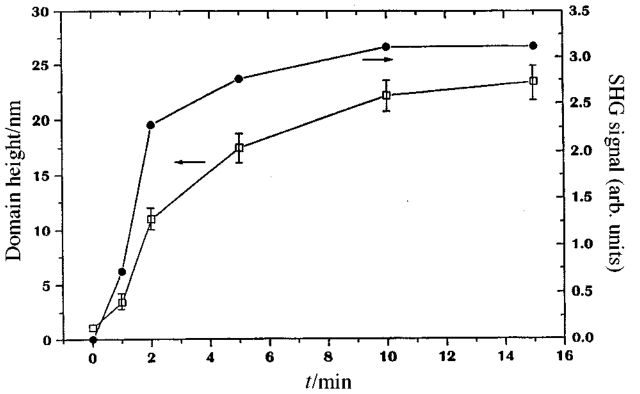

Fig. 2 SHG signal intensity and growth of the domains as a function of poling time measured after quenching at successive poling times at a poling temperature of 75 °C. The error bars were determined by repeating the measurement at five different positions on the same film.

noticeable decomposition at this poling condition. We believe this whitening is due to light scattering by chromophore domains of larger size formed during poling. One related observation for the same film is that relaxation of the SHG signal occurred by the progressive depression on the top of the domains removing the applied poling field. These results suggested that the domain size is apparently correlated with the observed SHG signal intensity.

It is interesting to note that a positive polarity was proven to work with our material much more efficiently than a negative one. When a negative polarity was applied, the observed SHG signal intensity almost vanished. The electric field in this polarity environment causes the axes of dipoles to be directed to the glass substrate, whose barrier effect hinders domain formation. In fact, the domains were not observed by AFM. A possible implication of this polarity effect is that the dipoles in this type of polymers can be oriented to form poled domains in cases where their alignment induced by the electric field facilitates cooperative movement of the rigid main chains. The attempted polings which failed confirmed this. When the corona poling was performed for films on which any barrier layers, including a vacuum deposited metallic electrode, were coated, the resulting SHG response was nearly absent, thus a sandwitch type poling was not adequate. However in cases where the films were corona poled first and then a barrier layer deposited on it, the SHG response remained almost unchanged and its temporal stability was greatly improved. This preliminary result may have important implications for obtaining stable materials for device applications. Design strategies to lock the domain itself would be valuable for improving geometrically the long term stability of second order NLO properties. We have also examined whether the roughened surface or interface had an important role in the measured SHG intensity by double coating the surface of the same polymer as the base film and then remeasuring the SHG intensity. We observed no loss in properties for this sample. This result indicates that the observed SHG should be related to the polar order effect of the chromophores in the domain rather than to the symmetry breaking nature of the roughened surface.

We have measured the SHG response of the samples for angles of incidence between −90 and 90° shortly after poling. The SHG signal of the polymer displayed no fringes, and only one peak indicative of thin sample films compared to the coherence length of the NLO process. In this case it is usual to determine the second order NLO susceptibility d_{33} by the curve fitting method using the intensity equation given by Jerphagnon and Kurtz.[6] We tried to determine d_{33} by fitting the data to the theoretical equation, but the result was not satisfactory and the experimental data systematically deviated from the theoretical values. However, the calculation at a single angle of 58° only resulted in a relatively large value of 50 pm V^{-1} referenced to a value of 0.3 pm V^{-1} for quartz, and the order parameter measured by the UV absorbance ratio was calculated to be 0.58, which to the best of our knowledge is higher than any reported values for poled polymer systems. It is still not clear if the fitting failure is a reflection of morphological changes in the polymeric films after poling. At this stage, it could be speculated that this behaviour is associated with the oriented domains largely formed on the outer surface layer and thus with the efficient second order NLO effect occurred only over a fraction of the film thickness. The SHG intensity against film thickness provides evidence of the inhomogeneous behaviour of chromophore orientations through the film thickness. As the thickness increased, the surface morphology became much rougher as a consequence of the larger sizes of the structure, and the more rugged the surface was, the greater the SHG intensity. However, the SHG intensity did not increase up to the level expected from the l^2 dependence[6] even when the film thickness was far smaller than the coherence length.

We gratefully acknowledge partial funding support from the Korea Science and Engineering Foundation (941-1100-011-2).

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Communication 8/06495D