Macromolecules **2002,** *35,* 4841−4844

Micropatterning of an Orienting Matrix Polymer with Nonlinear Optical Side Groups by Corona Poling

O-Pil Kwon, Doo-Jin Cho, Young-Hee Won, and Suck-Hyun Lee*

*Hyperstructured Organic Materials Research Center of
Seoul National University and Department of Molecular
Science and Technology, Ajou University,
Suwon, Korea 441-749*

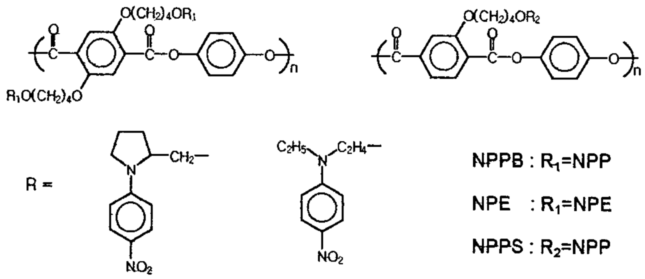
Received May 31, 2001
Revised Manuscript Received March 21, 2002

Introduction

The technological importance of polymeric materials lies mainly in their physical properties, and the everlasting question is to ask how the molecular structure is responsible for the observed macroscopic behavior. In second-order nonlinear optical (nlo) polymers, the kinetic growth and decay of the second-harmonic (SH) signal are closely connected to local intra- and intersegmental motions. This local motion is in turn related to the nature of the backbone chain or host polymer. Although there have been several recent studies involving rigid backbone systems for side group nlo polymers, most of the studies to date have been devoted to flexible backbone systems.[1−3] Fewer reports have discussed the poling dynamics of materials employing orienting polymer backbones. Recently, we have developed nlo polymers with large and stable second-order nonlinear susceptibilities where the nlo chromophores are covalently attached through a small spacer unit to rigid backbone polymers such as wholly aromatic polyesters or polyamides. We have observed for these materials the domain structure of chromophores formed after exposing thin films to the corona discharge.[4] They exhibit exceptionally good stability of the chromophore orientation at ambient temperature even though their T_g's are relatively low.[5] We attributed this temporal stability to the coupling between the chromophore and its anisotropic backbone environment.[6,7] In this study, we show the formation of micropatterned domain structures of nlo chromophores for an orienting matrix polymer by using a patterned electrode. To our knowledge, a patterning of nlo thin films by corona poling is reported for the first time. We also present the comparative studies on the patterning processes for the side chain polymers where the side groups are differently attached to the backbone while keeping the same backbone to gain a better understanding of polar ordering processes.

Experimental Section

Materials. The polymers used here are based on a rigid backbone polyester to which the nlo chromophores *N*-(4-nitrophenyl)-L-prolinol (NPP) are attached differently via flexible spacers. The structural formulas of the repeat unit are the following:



These polymers were prepared by the solution condensation of 2,5-disubstituted or 2-monosubstituted terephthalic acid chloride with hydroquinone. The details on the syntheses of the polymers were described elsewhere.[7] The inherent viscosity (IV) was measured at a concentration of 0.1 g/dL in tetrachloroethane. The IV values for the above three polymers of NPPB, NPE, and NPPS were controlled to be about 0.4, and their glass transition temperatures measured by differential scanning calorimeter were 70, 45, and 67 °C, respectively. The T_g is defined here as a starting point of the broad endotherm covering more than 50 °C. The observed low T_g's for these polymers are probably due to the broadened transitions associated with β relaxation of side groups and the conventional α relaxation of the main chains.

Patterning Procedure. Our patterning procedure begins with a fabrication of a transparent micropatterned electrode by interference lithography using an argon ion laser. We then use the spin-coating technique to prepare thin films on the patterned ITO glasses. Subsequently, they were corona-poled for 5 min at a temperature about 20 °C above T_g of the polymers. This poling temperature was selected according to the in-situ SHG experiments to maximize dipole alignment. We achieved the corona discharge in air by placing a positive voltage of 5 kV on a tungsten wire 1 cm above the film. After poling, the films were cooled to room temperature under the electric field maintained during the cooling process. The surface of the film was wiped with ethanol to remove any residual surface charges immediately after poling. We also studied the surface topographies of the spin-coated films before and after poling using atomic force microscopy (AFM). All AFM images were obtained with a Park Science Instruments Autoprobe LS operated in the contact mode in air.

SHG Measurements. Poling was performed in situ with the sample oriented at an angle of 45° to the incident beam path. SHG measurements were made using a Q-switched Nd:YAG laser operating at 1064 nm with a pulse repetition rate of 10 Hz. The p-polarized light was pulsed at an incidence angle 45° to the film surface, and a quartz reference signal was monitored concurrently to reduce laser fluctuations and correct for possible drifts in the laser intensity level.

Results and Discussion

Patterned Structures. When a dipolar molecular system is placed in an electric field, there is always the tendency for any dipoles to align along the field. Figure 1 shows the AFM surface profiles for the patterned electrode and the over-coated thin film. The original film surface before poling was quite smooth with hundreds of nanometer fluctuations in the depth due to the electrode layers protruded from the glass substrate. Figure 1c shows the topographic image of the poled film for the sample containing two side groups per repeat structure of the base polymer designated NPPB. It revealed a striped structure having gaps between adjacent domains with dimensions of about 1.5 μm, half of the width of the electrodes. The depth of the surface

10.1021/ma0109471 CCC: $22.00

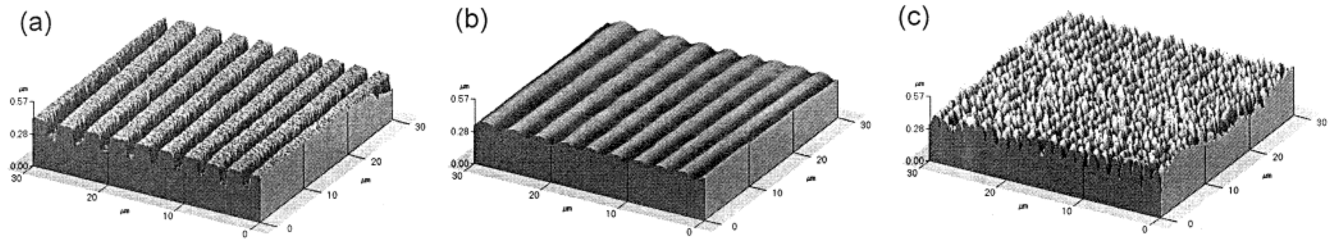
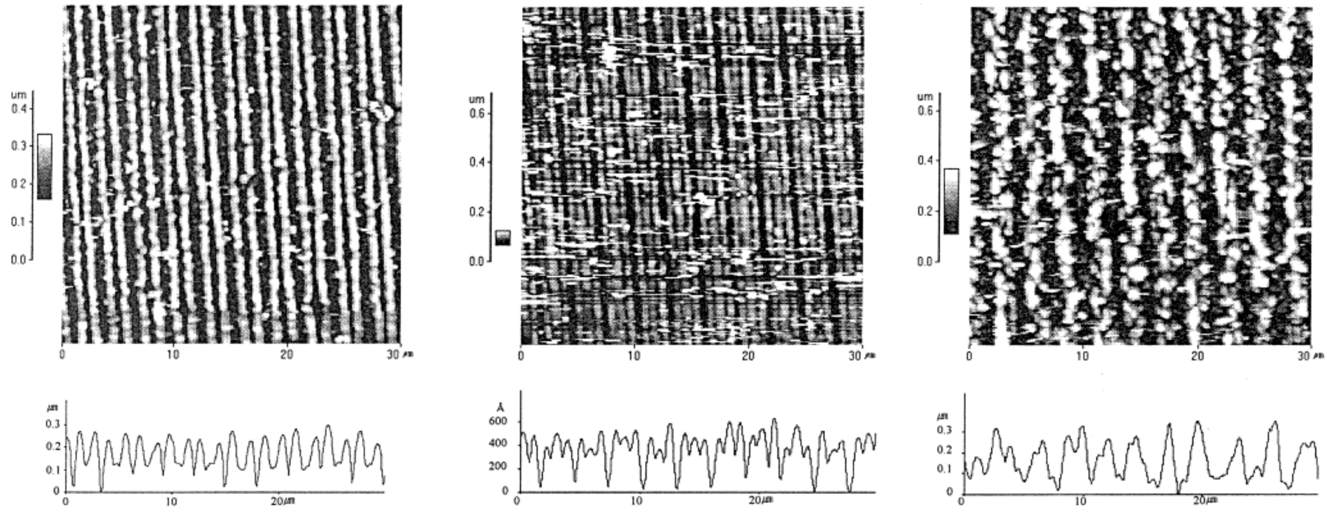


Figure 1. AFM images for a patterned electrode (a) and over-coated thin films for NPPB before (b) and after (c) corona poling (92 °C, 5 kV, 5 min).



(a) NPPB (b) NPE (c) NPPS

Figure 2. AFM two-dimensional images and their height profiles for a poled film of NPPB (a), NPE (b), and NPPS (c).

relief patterns was about 120 nm, which was approximately 20% of the original film thickness (0.6 μm). These patterns look similar to those obtained by Nathansohn et al. and Tripathy et al., whose processes involve repeated trans−cis photoisomerization of azobenzene groups and thermal relaxation resulting in the alignment of azobenzene groups in the direction perpendicular to the polarization of the incident light.[8] Our method is different from theirs. We think that the above-patterned structures are a result of the pumping action by nonuniform electric fields. Nonuniform fields are produced here not only in the corona field but also in the vicinity of sharp point or line sources. For example, the field varies as $1/r$ at the edges of line electrodes;[9] hence, the dielectrophoretic force would be expected to increase by the grad$(E)^2$ or $1/r^3$ at the edges. We believe that the intense local fields at the sharp edges of the grounded ITO electrode layer (Figure 1a) gave rise to the observed patterned structure. The electric field in this polar environment caused the axes of dipoles to be directed upward, and the polymer backbones responded by changing their contours locally to adapt to the uniaxial distribution of the poled chromophores. The result was the creation of the patterned domains, orientationally biased chain contours among the poled chromophores.

To examine whether the polymer backbone and the mode and extent of chromophore attachment play a significant role in the patterning of these domain forming polymers, we have additionally prepared the same backbone polymer with differently attached NPP chromophore units. From the sample designated NPE, where the chromophoric groups were longitudinally attached to the backbone using conventional amine containing chromophores instead of a prolinol connection, we observed the different domain structures. The topographic image analysis revealed much smaller domain heights on the order of tens of nanometers, and additional mounds between the edges appeared due to the smaller depression on the original top surfaces as evinced by the topography shown in Figure 2b. This difference suggests that the prolinol linking groups in the former polymer provide a “jacketed” effect on the backbone, resulting in a larger scale motion of the backbone chains. When the chromophores are incorporated into the polymer side chains with the dipole moment of the chromophore placed parallel to the molecular axis of the polymer backbone, the parallel component of the dipole is coupled to the chain contour in a head-to-tail arrangement. Thus, the alignment of adjacent backbone segments assists the dipole addition during electric poling, and the observed domain itself may be viewed as a single giant molecule with a superdipole, which leads to enhanced second-order nlo properties.[5,9] These jacketed effects would be less marked when decreasing the level of substitution. Figure 2c shows the topographic image for the same backbone polymer having only one pendent group per formula unit designated NPPS. As expected, the domain structures are not well developed, and the quality of the patterned structures is much lower than that of the patterns generated for the polymer NPPB. However, the final size of the domains in depth is comparable for the two samples of NPPB and NPPS. We will see below that it

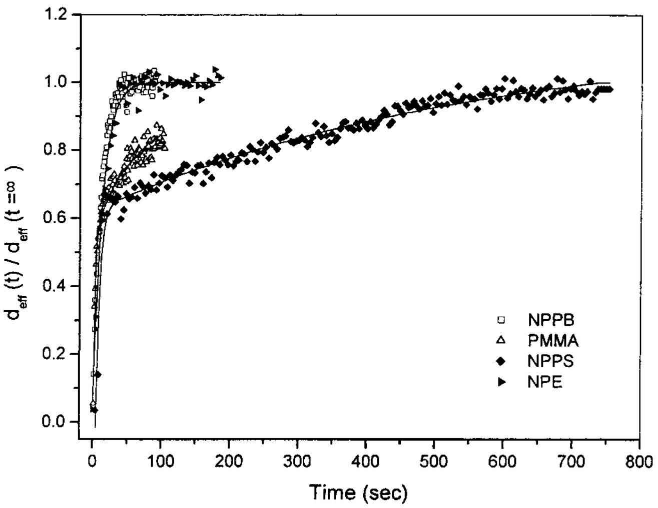


Figure 3. Corona poling field-induced growth of the SHG signal against time obtained during the first poling from the different polymers: NPPB (□), NPE (▼), NPPS (◆), and PMMA (△).

Table 1. Comparison of Parameters Obtained by Fitting the Square Root of the Growth Intensities of the SHG Signal for the Polymers

	first poling				second poling			
	τ_1	a_1	τ_2	a_2	τ_1	a_1	τ_2	a_2
NPPB	11.31	1.21			5.15	1.25		
NPE	13.60	1.64			3.22	4.57		
NPPS	556.21	0.65	5.40	1.70	2.45	5.67		
PMMA	42.09	0.32	1.80	0.80	46.03	0.22	3.02	0.69

takes much longer periods of time for the NPPS to reach this final orientation.

Poling Dynamics. Another interesting aspect of these domain-forming polymers is in their dynamic behaviors. On the basis of a large amount of SHG experiments using various polymers, the rise and decay in the SH signal turned out to depend on the attaching mode of side groups. We report in this study on the poling dynamics for these orienting backbone polymers and compare them with a flexible backbone system, the PMMA system ($T_{\rm g} = 83$ °C, poling temperature $= 90$ °C). The same chromophores, NPP, were covalently attached to the PMMA backbone with a content of about 42 wt %, comparable to the content in NPPB. Figure 3 shows the growth curves of the SHG signal with poling time for the four types of side group polymers as mentioned above. The vertical axis is the square root of the SHG intensity of the samples normalized to a quartz reference. The values plotted are also relative to the initial intensity to compare the transients of all the compounds. Comparison of the transients shows that the SHG rises similarly in the two samples, NPPB and NPE, and approaches the asymptote at a much faster rate compared with that of the sample NPPS. Quantitative examination of Figure 3 revealed that the growth of the SHG signals can be described by a monoexponential function for the orienting matrix polymers, NPPB and NPE (Table 1). In the case of the NPPS and PMMA system, we have observed a two-step rise as was discussed by numerous authors.[10−19] The two-step rise has been generally interpreted as follows: the short time process described by τ_1 of a few seconds is related to the fast reorientation response of the uncorrelated side group chromophores which are free to rotate. The subsequent slow growth of the SHG signal described by τ_2 is due to an improved alignment of chromophores resulting from polymer chain contour rearrangements. We confirmed that the temporal characteristics observed for the PMMA sample were consistent with the above interpretations. In the case of the NPPS, the side group chromophores are attached to the backbone in a nonsymmetric manner because of single substituent per repeat structure. Therefore, a rapid orientation of the chromophores in the film surface led to the nearly instantaneous growth of the SHG. However, it is difficult to use this two-step growth model to account for the growing pattern observed in the orienting backbone polymers whose process fits to a single exponential.

It is quite surprising that the poling dynamics for the orienting backbone system are completely dominated by a single-exponential rise considering rotational mechanisms linked to the chromophores and the backbone. The physical grounds of this process are not clearly understood yet, but it seems that the rigid backbone environment results in a dominance of completely coupled motions between the backbone and the side groups. It should be noted that the film preparation by spin-coating resulted in somewhat disentangled planar orientation of the rigid backbones.[5] As a result, the polar ordering of the chromophore dipoles occurred only when the rigid backbone segments were able to respond simultaneously by changing their local conformations to adapt to the anisotropic orientation distribution of poled chromophores. For an example, a sandwich type poling was not suitable for this material according to our previous studies[3] because the covering rigid electrode layer inhibited the upward motion of the planar backbone chains. In addition, orientationally biased chain contours among the poled chromophore dipoles (we designate them domains) are created on the surface by only an upward force toward the region of higher field intensity.[3] It is also interesting to note that the mountainlike domain structures protruded above the film surface clearly excludes the possibility of single rate process arising from noncooperative local free motions of the side groups without any main chain coupling. It is therefore reasonable that complete main chain coupling with cooperative chromophore motions results in one rate process, not incorporating additional mechanisms such as ultraslow reorientation motions of the chromophores in liquid crystalline polymers (τ_3).[14] Recently, we have confirmed this completely coupled motion between the backbone and the side groups in ultrathin films by in-situ surface enhanced Raman spectroscopy.

Also of interest in Figure 3 is the time for the SHG intensity to reach its maximum value. According to Table 1, the characteristic time in the NPPS (556 s) is much longer than the time in the other samples (11−13 s). We notice that, undoubtedly, decreasing the amount of chromophores leads to a longer poling time. This lengthening effect would be due to smaller dielectrophoretic forces by a single chromophore per repeat unit for this polymer. The striking feature is that its poling behavior during the second poling is very similar to the other orienting polymers. After the SHG signal induced in the first poling had decayed to an undetectable level, the poling process was repeated under identical conditions for all the samples. According to the results, the general features only in the NNPS sample were changed to single-exponential growth, and the rise

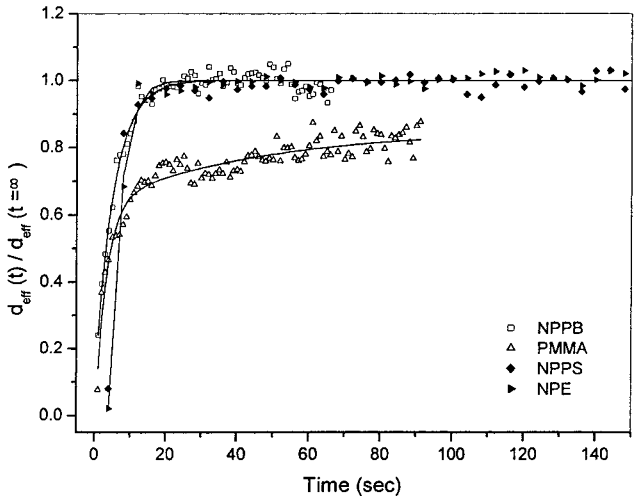


Figure 4. Corona poling field-induced growth of the SHG signal against time obtained during the second poling from the different polymers studied: NPPB (□), NPE (▼), NPPS (◆), and PMMA (△).

time was drastically decreased (Figure 4). Since the interval between the decay and rise was too short for a rigid chain contour to undergo significant rearrangements, the local environment of the orienting backbone polymers shifted during the first poling to conform to the oriented domains, resulting in a more rapid growth than during the first poling.[15]

These results suggest that, on poling and relaxing with electric field, main chains acted as an mobile layer species easily moving up and down and poling took place in the direction perpendicular to the face of the film. The memory effect by trapped charges as discussed by Pauley et al.[13] in the guest−host PMMA system is believed to be negligible in our experiment because the PMMA sample took a longer time to establish the plateau SHG signal during the second poling under similar conditions.

Conclusion

In this study, we showed the micropatterned domain structures of nlo chromophores obtained using a patterned electrode by corona poling. The results indicated that the patterned domain structures and poling dynamics depended on the mode and extent of side groups attached to the orienting backbone. Patterned structures were particularly well developed for a sample with two chromophores per repeat structure of the backbone connected by a prolinol group. The poling dynamics were different for the different samples. A two-step rise was observed in the case of the NPPS (single substitutent/monomer) and the flexible backbone system of PMMA, whereas for the rigid backbone systems (symmetric double substitutents/monomer), the poling dynamics were completely dominated by monoexponential rise. These results were discussed in terms of the orienting backbone environment where a complete coupling of motions occurs between the main chain and the nlo side group chromophores.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-1999-015-D10044).

References and Notes

(1) Dalton, D. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, A. K. Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060.
(2) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.
(3) Wise, D. L.; Wnek, G. E.; Trantolo, D. J.; Cooper, T. M.; Gresser, J. D. *Photonic Polymer Systems*; Marcel Dekker: New York, 1998.
(4) Lee, S. H.; Kang, Y. S.; Song, S. J. *Chem. Commun.* **1998**, 2513.
(5) Lee, S. H.; Lee, J. W.; Kwon, O. P.; Lee, C. H.; Won, Y. H. *Appl. Phys. Lett.* **1999**, *74*, 2067.
(6) Lee, S. H.; Kim, Y. K.; Won, Y. H. *Macromolecules* **1999**, *32*, 342.
(7) Lee, S. H.; Kim, C. K.; Kwon, O. P.; Lee, M. W.; Won, Y. H. *J. Polym. Sci., Polym. Phys. Ed.* **1999**, *37*, 3108.
(8) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 553. (b) Kim, D. Y.; Li, L.; Jeng, R. J.; Kumar, J.; Fiddy, M. A.; Tripathy, S. K. *SPIE Proc.* **1993**, *23*, 1853.
(9) Pohl, H. A. *Dielectrophoresis*; Cambridge University Press: New York, 1978; p 481.
(10) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 3648.
(11) Firectone, M. A.; Ratner, M. A.; Marks, T. J. *Macromolecules* **1995**, *28*, 6296.
(12) Boyd, G. T.; Francis, C. V.; Trend, J. E.; Ender, D. A. *J. Opt. Soc. Am. B* **1991**, *8*, 887.
(13) Pauley, M. A.; Wang, C. H.; Jen, A. K. Y. *Macromolecules* **1996**, *29*, 7064.
(14) Kajzar, F. *Nonlinear Opt.* **1999**, *20*, 53.
(15) Wang, H.; Jarnagin, R. C.; Samulski, E. T. *Macromolecules* **1994**, *27*, 4705.
(16) Hayden, L.; Sauter, G.; Ore, F.; Pasillas, P.; Hoover, J.; Lindsay, G.; Henry, R. *J. Appl. Phys.* **1990**, *68*, 456.
(17) Kuzyk, M.; Singer, K.; Zahn, H.; King, L. *J. Opt. Soc. Am. B* **1989**, *6*, 742.
(18) Firestone, M. A.; Ratner, M. A.; Marks, T. J. *Macromolecules* **1995**, *28*, 6296.
(19) Liu, L. Y.; Ramkrishna, D.; Lackritz, H. S. *Macromolecules* **1994**, *27*, 5987.

MA0109471