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Low temperature relaxations and effects on poling efficiencies of dendronized nonlinear optical side-chain polymers

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Low temperature relaxations in a dendronized nonlinear optical (NLO) side-chain polymer were found to take place at more than 20 °C below the glass transition temperature. Relaxations of localized mobilities, removed from long range relaxations responsible for chromophore aggregation, are shown to offer new gateways for optimized acentric ordering of the chromophores. Supreme electro-optical (EO) activity was achieved by electrical poling close to the critical temperatures of localized mobilities identified as dendronized NLO side-chain relaxations. This study features, in particular, one new instrumental approach to relaxation studies of thin spin coated NLO polymer films; the shear-modulation force microscopy (SM-FM) method. Originating from scanning force microscopy (SFM), the SM-FM method grants access to the detection of low temperature relaxations in constrained thin NLO films not obtainable by conventional means. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1938005]

Organic second order nonlinear optical (NLO) materials have been heavily investigated for their potential applications in electro-optical (EO) modulators and frequency-doubling devices.[1,2] One of the impediments for obtaining highly efficient NLO materials lays in the translation of high molecular nonlinearity into the phenomenological EO activity by poling-induced acentric ordering of the chromophores.[3] Acentric ordering of the chromophores is commonly achieved by electric field poling at elevated temperatures. In particular, it is common practice that the poling process is executed at or above the glass transition temperature, T_g.[4] In the case of chromophore guest-host systems, the T_g value of the host material determines the mobility of the chromophores,[2,5] and thus, serves as a convenient parameter for assessing the poling temperature. While the T_g value of the host material is a suitable poling parameter for most guest-host NLO systems, it is inappropriate for constrained materials, such as dendronized NLO side-chain polymers, i.e., materials with a chromophore-incorporated macromolecular structure.

The polystyrene-based NLO polymer, PS-CLD1,[6] illustrated in Fig. 1, is a dendronized NLO side-chain polymer. For enhancement of the EO activity and the thermal stability, highly nonlinear CLD-type[7] chromophores and bulky dendrons were covalently attached onto the polystyrene backbone and the chromophores. A major difficulty that arises with such complex macromolecular structures is the determination of an appropriate poling temperature. In this letter, we will show that a critical rheological relaxation within the bulky structure, at a temperature tens of degrees below the glass transition temperature, offers an optimal condition for electrical poling. As this low temperature structural relaxation is not observable by conventional methods, e.g., differential scanning calorimetry (DSC), this study involves a nanoscopic mechanical method that has recently been introduced for inter- and intramolecular relaxations; the shear modulation force microscopy SM-FM.[8] In addition, lateral force microscopy (LFM) is applied to investigate the effect of aggregation on the poling efficiency in terms of the thermal history and the poling temperature.

The dendronized NLO side-chain polymer, PS-CLD1 was synthesized utilizing a post-functionalization reaction.[6] For poling and thermomechanical characterization, thin films were spin cast from a 13% PS-CLD solution dissolved in cyclopentanone (filtered through 0.2 μm syringe filter) onto indium tin oxide (ITO) coated glass substrates. The resulting films, with thickness on the order of 1 μm, were annealed at 85 or 100 °C in a vacuum oven (Napco Model 5851) for over 12 h. Electrical poling was conducted at 130 V/μm for all samples. EO activity coefficients, r_{33}, representing the degree of chromophore alignment, were obtained using the Teng and Mann reflection technique at 1.3 μm.[9] A stand-alone scanning force microscope (Explorer, Veeco Instruments) was used for scanning lateral force (LFM) and non-scanning contact stiffness (SM-FM) measurements. Both methods involved nanometer sharp SFM cantilever tips

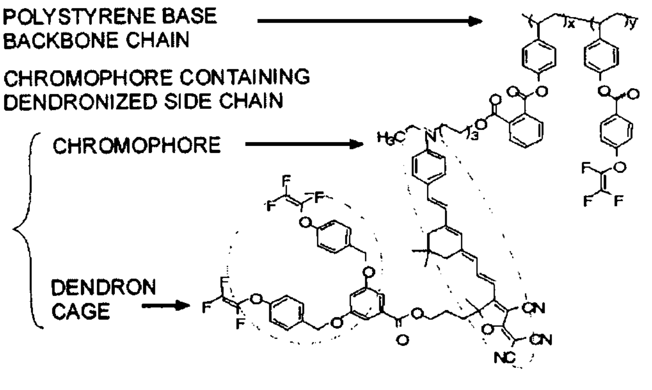

FIG. 1. Chemical structure of the dendronized NLO polymer, PS-CLD1 (Ref. 6). The dendron moiety is attached to the chromophore containing side chain that is connected to the polystyrene base backbone.

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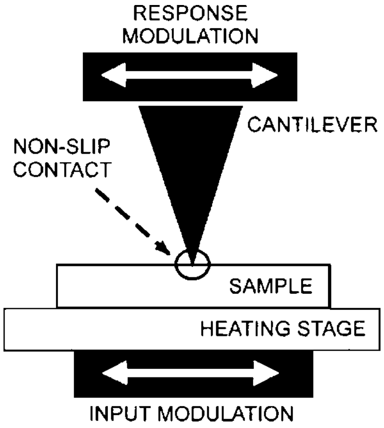

FIG. 2. Schematics of shear modulation force microscopy (SM-FM).

(NanoSensors™, normal spring constant of 0.092 N/m). The LFM yields annealing temperature-dependent friction coefficients used to interpret the degree of chromophore aggregation. Rheological relaxations in the spin cast films were obtained by SM-FM.[8,10,11]

The SM-FM method,[11] depicted in Fig. 2, entails a nanometer sharp scanning force microscopy (SFM) cantilever tip, which is brought into contact with the thin film surface. While a constant load is applied, the probing tip is laterally modulated under no-slip condition, i.e., small enough amplitude that guarantees no relative probe-sample motion. The response amplitude, a measure of the contact stiffness, k_c, which is a function of the materials' moduli and contact dimension, is recorded. For an inert sampling tip, changes in k_c reflect rheological changes in the sample material. It has been demonstrated that thermally activated structural transitions, such as the glass transition, are causing significant variations, i.e., "kinks," in the response curve.[10,11]

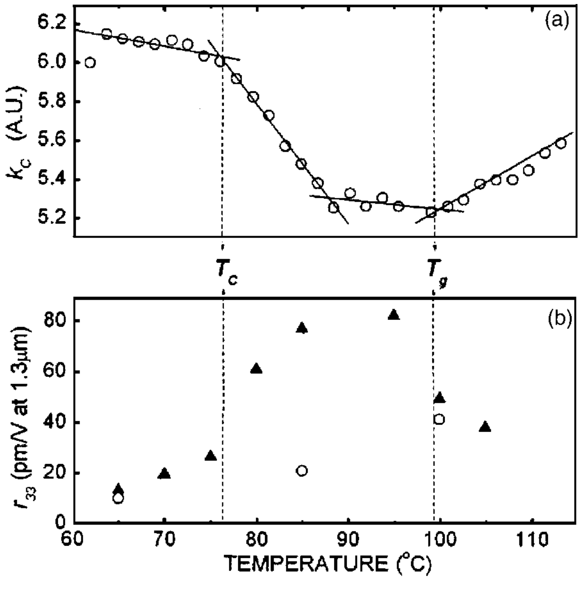

FIG. 3. Thermomechanical relaxations at T_c and T_g and their effect on the poling efficiency: (a) contact stiffness k_c of PS-CLD1, determined by SM-FM, reveals both critical relaxation temperatures, T_c and T_g; (b) corresponding EO activity coefficients, r_{33}, for samples annealed at 85 °C (▲) and 100 °C (○).

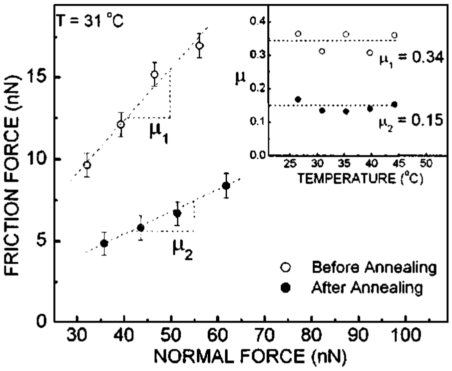

FIG. 4. Representative shear mechanical studies (friction) before (○) and after (●) thermal annealing of PS-CLD1 at T=31 °C. (Inset) Friction coefficients before (μ_1=0.34) and after (μ_2=0.15) annealing determined in the glassy state of PS-CLD1, and temperature averaged over 26–44 °C.

A SM-FM analysis of a thin film of PS-CLD1 reveals two transitional "kinks," Figure 3(a), one at T_c=77±1 °C followed by one at T_g=99±1 °C. Only the second one could be observed by DSC and corresponds to the glass transition temperature of PS-CLD1. From the viewpoint of contact mechanics, the SM-FM result can be interpreted as follows: At T=77 °C, the contact stiffness decreases after the kink, because the material's shear modulus decreased but the contact area has remained the same. Such a transition describes a structural reorganization within the material that does not affect the internal pressure. At T=99 °C, the contact stiffness increases because of an increase in the contact area. This is a more common observation for polymer films that experience a glass transition, where the internal pressure of the sample drops significantly, and the sampling tip sinks in until the contact area is increased to such a degree that the pressure is equilibrated. Typically, changes in the contact area dominate changes in the modulus in nanoexperiments.

The qualitative behavior of the transition at T_c suggests that the smaller moieties, i.e., the side chains, are relaxing. Guided by this finding, we have investigated the effect of the poling temperature in relation to T_c and T_g. It can be inferred from Fig. 3(b) that the EO coefficient, r_{33}, significantly increases above T_c, thus, leading to improved poling efficiency. This finding supports our addressed SM-FM based interpretation of side chain relaxation. The observed decrease in r_{33} above T_g can be explained by an increase in the aggregation of chromophores, and/or degradation due to high voltage/high temperature poling. To confirm thermally induced aggregation effects, the poling efficiency of PS-CLD1 samples that were annealed above T_g; i.e., 100 °C, were compared to the one obtained from samples that were annealed at a temperature within the range of T_c and T_g; i.e., at 85 °C. For samples poled at 85 °C, the film annealed above T_g revealed only 17% of the r_{33}-value compared to the film annealed at 85 °C, Fig. 3(b). Evidently, exposing the sample to temperatures above T_g promotes undesired chromophore aggregation. These results compare well with EO values obtained for samples poled above T_g, as illustrated in Fig. 3(b). Thus, the abrupt drop in r_{33} at the glass transition is mainly due to thermally induced aggregation and is not caused by chemical degradation.

Additional support regarding the aggregation of chromophores in thin NLO films within 26 and 44 °C (glassy state) was provided by LFM. The lateral force analysis, involving the friction coefficient μ, has been shown to be a very effective tool for detecting relative structural differences in thin films.[12] Figure 4 shows that a film annealed at 85 °C reveals a friction coefficient μ_1 of 0.34. After exposing the same film to a temperature above T_g, i.e. 133 °C, the friction coefficient was reduced by over 50% to μ_2 of 0.15. Since a reduction in the friction coefficient is indicative of an increase in the elastic modulus for constant adhesive force,[13] the friction data support the interpretation of enhanced but undesired chromophore coupling above T_g.

In summary, optimized acentric ordering of the chromophores in a constrained dendronized NLO guest-host system, was achieved by nanoscopic analyses of the relaxation properties. While generally the T_g value of the material is considered to be a suitable poling parameter, this study showed it to be inappropriate. The dendronized NLO side-chain polymer PS-CLD1 exhibited a low temperature relaxation that takes place at more than 20 °C below T_g at T_c. Thereby the EO activity was shown to be significantly raised at T_c. The merit of *low temperature poling* and annealing has been discussed in terms of undesired chromophore aggregation, which was significantly higher at T_g compared to T_c. This study featured, in particular, one new instrumental approach to relaxation studies of thin spin coated NLO polymer films; the SM-FM method. This method provided both T_c and T_g in a single sweep experiment, while only T_g was obtainable by conventional means.

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[1] L. R. Dalton, B. H. Robinson, A. Jen, W. H. Steier, and R. Nielsen, Opt. Mater. (Amsterdam, Neth.) **21**, 19 (2002); H. Ma, S. Liu, J. Luo, S. Suresh, L. Liu, S. H. Kang, M. Haller, T. Sassa, L. R. Dalton, and A. K.-Y. Jen, Adv. Funct. Mater. **12**, 565 (2002); S. R. Marder and J. W. Perry, Science **263**, 1706 (1994); T. J. Marks and M. A. Ratner, Angew. Chem., Int. Ed. Engl. **34**, 155 (1995).

[2] R. D. Dureiko, D. E. Schuele, and K. D. Singer, J. Opt. Soc. Am. B **15**, 338 (1998).

[3] B. H. Robinson and L. R. Dalton, J. Phys. Chem. A **104**, 4785 (2000); F. Kajzar, K.-S. Lee, and A. K-Y. Jen, Adv. Polym. Sci. **161**, 1 (2003).

[4] H. Ma, A. K.-Y. Jen, and L. R. Dalton, Adv. Mater. (Weinheim, Ger.) **14**, 1339 (2002); I. Teraoka, D. Jungbauer, B. Reck, D. Y. Yoon, R. Twieg, and C. G. Willson, J. Appl. Phys. **69**, 2568 (1991); H-J. Winkelhahn, T. K. Servay, and D. Neher, Phys. Chem. 100, 123 (1996).

[5] D. M. Burland, R. D. Miller, and C. A. Walsh, Chem. Rev. (Washington, D.C.) **94**, 31 (1994).

[6] J. Luo, S. Liu, M. Haller, L. Liu, H. Ma, and A. K.-Y. Jen, Adv. Mater. (Weinheim, Ger.) **14**, 1763 (2002).

[7] Y. Shi, C. Zhang, H. Zhang, J. H. Bechtel, L. R. Dalton, B. H. Robinson, and W. H. Steier, Science **288**, 199 (2000); C. Zhang, L. R. Dalton, M. C. Oh, H. Zhang, and W. H. Steier, Chem. Mater. **13**, 3043 (2001).

[8] T. Gray, C. Buenviaje, L. Zheng, S. A. Jenekhe, A. K-Y. Jen, and R. M. Overney, Appl. Phys. Lett. **83**, 2563 (2003).

[9] C. C. Teng and H. T. Man, Appl. Phys. Lett. **56**, 1734 (1990).

[10] S. Ge, Y. Pu, W. Zhang, M. Rafailovich, J. Sokolov, C. Buenviaje, R. Buckmaster, and R. M. Overney, Phys. Rev. Lett. **85**, 2340 (2000); S. Sills and R. M. Overney, J. Chem. Phys. **120**, 5334 (2004).

[11] R. M. Overney, C. Buenviaje, R. Luginbuehl, and F. Dinelli, J. Therm Anal. Calorim. **59**, 205 (2000).

[12] R. M. Overney, G. Tindall, and J. Frommer, in *Handbook of Micro/Nano Tribology*, edited by B. Bhushan (Springer, Heidelberg, 2003).

[13] C. Buenviaje, F. Dinelli, and R. M. Overney, Macromol. Symp. **167**, 201 (2001).