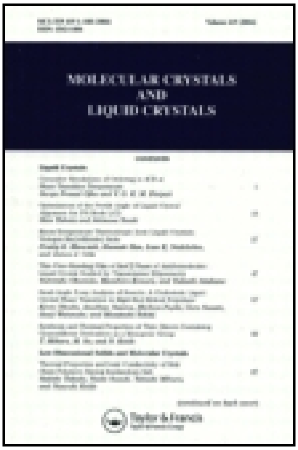

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Rigidity Dependence of Alignment and Relaxation in Main-Chain Nonlinear Optical Polymers Measured by Optical and Electrical Method

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The dynamics of two main-chain nonlinear optical polymers, PA-PS and PA-MS, was studied at various temperatures below T_g. In the characterization, both the photo-induced isomerization method and second harmonic generation were employed. In the case of non-polar alignment by the linearly polarized UV light, the main-chain of PA-PS polymer was found well re-aligned but the main-chain of PA-MS polymer was not, because of the high rigidity. In the case of polar alignment by *in-situ* corona poling technique, double exponential functions fit well to the data of both PA-PS and PA-MS polymer relaxation data at all the temperature range.

Keywords: main-chain polymer; photoisomerization; relaxation dynamics

INTRODUCTION

Nonlinear optical (NLO) organic materials have been intensively investigated because of their potential applications to photonics devices such as second harmonic generator, phase conjugator, optical switch, and EO modulator. The study of alignment dynamics of the chromophore as well as the polymer main-chain is important in characterizing the polymeric materials for the devies application. In this work, the dynamics of two main-chain nonlinear optical polymers, PA-PS and PA-MS, having different glass transition temperatures, hence different rigidities, was studied at various temperatures below T_g. In the characterization, both photo-induced isomerization method and second harmonic generation were employed. From the infrared (IR) spectroscopy, we observed that the locomotive motion of polymer main-chain is present.

EXPERIMENT

Sample preparation: Figure 1 shows two newly synthesized main-chain polymer structures which were PA-PS (Poly[2-(2-(4-(dimethylamino)phenyl)vinyl)-5-nitro-1,4-phenylene] imino-[bis(4-carbonylphenylene) diphenylsilane] imino)] and PA-MS ([Poly (2-(2-4-(dimethylamino)phenyl)vinyl)-5-nitro-1,4-phenylene]-imino-[bis(4-carbonyl-phenylene) dimethylsilane] imino)]. The glass transition temperatures of PA-PS and PA-MS are 111°C and 176°C, respectively. The different polymer main-chain structures are responsible for the different glass transition temperatures of PA-PS and PA-MS. To prepare the thin film, two main-chain polymers were dissolved in *N*-methly-2-pyrrolisone (NMP) at 10 weight %. The solutions were stirred for one day at room temperature and filtered with a 0.2μm teflon filter. Thin films on a clean slide glass and sapphire slide were spin coated at 400rpm for one minute. The sapphire slides allow spectroscopic measurement of IR region (1400-2000 cm^{-1}). The solvent was removed under vacuum condition at 110°C for 10 hours.

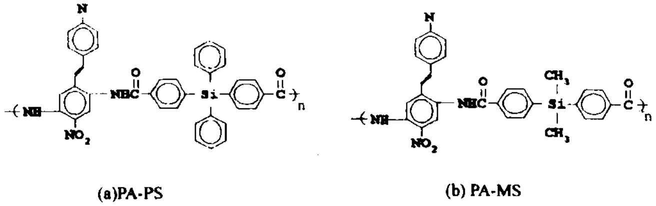


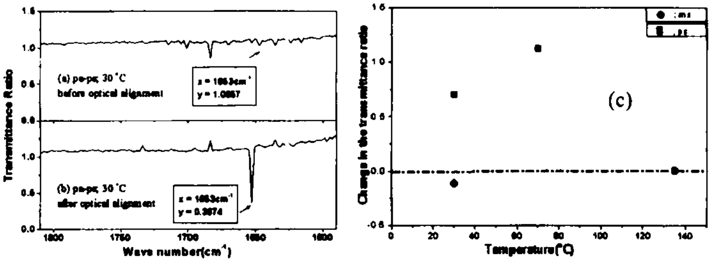
FIGURE 1 Main-chain nonlinear optical polymer structures; (a) PA-PS and (b) PA-MS

Measurement of photo-induced alignment: Since the chromophore of the polymer possesses stilbene, it can be aligned through the photo-isomerization process in the desired direction by pumping with a polarized UV light. Optical pumping was carried out by irradiating the samples on sapphire substrate with a linearly polarized UV light from 1kW mercury lamp which is band pass filtered, and lens focused. The samples were pumped for one hour at room temperature and T_g-40°C respectively, and then IR spectra were obtained right after.

***In-situ* measurement of the transient NLO response:** For the electric-field poling of chromophores, we employed a corona poling method, the same as that reported in our previous work [1]. The corona poling voltage of 3.5kV was applied evenly on the sample and the distance between tungsten tip and ITO electrode was 1.5cm.

RESULTS AND DISCUSSIONS

It has been known that the photo-isomerization of stilbene groups results in the rearrangement of polymer main-chain. To confirm this, IR spectra were taken to measure the photoinduced alignment of polymer main-chain. We observed the change in the ratio of C=O stretching vibration mode, perpendicular to parallel direction of pumping light polarization, at 1653cm^{-1} of polymer main-chain [2], which shows that the alignment of polymer main-chain is achieved by optical pumping for PA-PS [Fig. 2(a) and (b)]. Figure 2(c) shows the IR-transmission ratio change at 1653cm^{-1} of the PA-PS and PA-MS before and after optical pumping at the temperatures of 30℃ and T_g-40℃.



FIFURE 2 IR-transmission spectra ratio of the PA-PS (a)before and (b)after optical pumpin at 30℃, and (c)IR-transmission ratio at 1653cm^{-1} of the PA-PS (■) and PA-MS(●).

It was found that the PA-PS polymer was aligned well and the amount of alignment increases as temperature increases. However, the main-chain of PA-MS is not aligned well by optical pumping. From the comparison of glass transition temperature of the two polymers, we conclude that the alignment of PA-MS is restricted by the rigidity of polymer main-chain. In order to investigate the dynamics of dipoles in main-chain polymers, we performed the *in-situ* second harmonic generation measurement with a corona field applied at the temperatures of 30℃, T_g-40℃, and T_g-25℃ for each sample. We observed the polar alignment for both PA-PS and PA-MS, which occurs in the molecular dipoles as well as in the polymer main-chain. The relaxation dynamics were investigated upon removing the corona electric field. At all the temperature range, both double exponential function and Dissado-Hill many body model fit well to the data of both PA-PS and PA-MS polymer except the data of PA-PS at 30 ℃ in which case only the double exponential function fits well [Fig. 3 (a)-(d)].

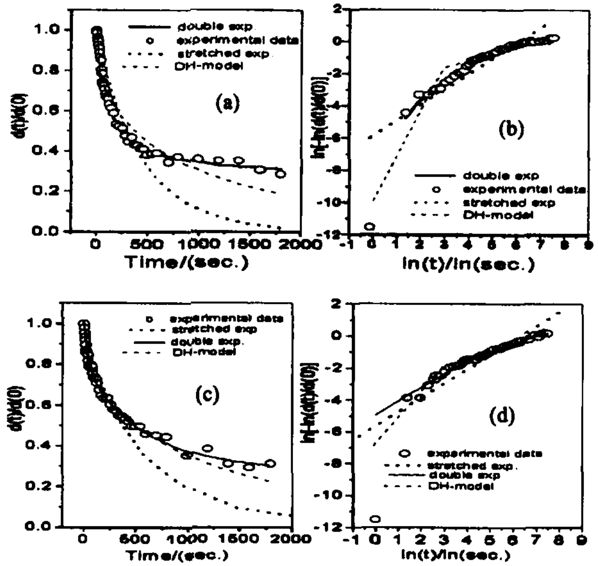


FIGURE 3 The relaxation dynamics; for the PA-PS sample (a) the plot of d(t)/d(0) *vs*. t and (b) the plot of ln[-ln(d(t)/d(0))] *vs*. ln(t) at 30 °C and for the PA-MS sample (c) the plot of d(t)/d(0) *vs*. t and (d) the plot of ln[-ln(d(t)/d(0))] *vs*. ln(t) at 30 °C.

We observed that the polar alignment (an external corona field) can be achieved for both PA-PS and PA-MS main-chain, while the non-polar alignment (optical pumping) can be achieved for PA-PS only.

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