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Second harmonic generation studies of intrinsic and extrinsic relaxation dynamics in poly(methy1 methacrylate)

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ABSTRACT

Second harmonic generation (SHG) is used to monitor the reorientation a dopant chromophore in slightly entangled poly(methy1 methacrylate) (PMMA). The effect of charge and temperature on both the decay and the much less studied onset modes of SHG signal at temperatures above the glass transition has been examined. At variance with the theoretical predictions, it is shown that the onset and the decay times are not coincident. An isothermal experiment above the glass transition shows a lengthening of relaxation time of the decay mode due to successive poling process, which is ascribed to charge memory effects. In contrast, the latter do not affect the onset characteristic time. The effect of temperature above the glass transition on dopant rotation and polymer relaxations has been also examined. As temperature increases the relaxation times of both the onset and the decay modes decrease. If the surface charge and the charge memory effect are erased, the decay time compares quite well with the structural relaxation time. Differently, the onset time exhibits a partial decoupling.

1. Introduction

Polymer molecular systems are complicated and difficult to study, even in this modern age. Nowadays, there is big effort to understand mechanical and electrical behavior of these systems and many experimental methods are developed for this reason. Laser spectroscopy techniques are excellent methods to study fast and slow dynamics of the complicated polymeric systems. In our present work we used SHG (second harmonic generation) method that deals with non-linear optical properties of guest–host polymer.

The study of polymers for SHG, the conversion of light of frequency ω to 2ω, is over two decades old [1–4]. The interest in using polymers for second-order non-linear optics (NLO) is related to the production of inexpensive alternatives to inorganic crystals for frequency doubling in laser and optical data storage applications and for electro-optic devices [5–7]. It is important to note that knowledge of the temporal and thermal stability of the SHG intensity is required for device applications of these polymeric NLO materials such as spatial light modulators, waveguides, and optical switches. A major stumbling block in the application of polymers for SHG has been the temporal decay [8] of the second-order macroscopic susceptibility, $\chi^{(2)}$, related to the square root of SHG intensity; this temporal decay is evident in glassy thermoplastics and thermosets containing doped [8,9] or covalently attached [10] NLO chromophores. In order to obtain SHG properties in an amorphous polymer, it is necessary to make the polymeric system noncentrosymmetric by applying a poling field, resulting in a net orientation of NLO chromophore dipoles [1]. However, upon removal of the poling field, randomization of NLO chromophore orientation occurs over time [8], resulting in a decrease in $\chi^{(2)}$ and SHG intensity.

Apart from application, SHG technique is also a powerful technique to investigate the polymer dynamic. Many optical techniques [11–13] have been used to examine dopant orientation or rotation in glassy polymers. Fluorescence anisotropy [11] can be used to study glassy behavior on a molecular level but is limited in studying temporal changes in the material due to the

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length of time required to obtain each data set. In contrast, the SHG experiment can be used to measure dopant orientation and NLO properties continuously over a wide variety of time scales and a range of temperatures from well below to well above the glass transition temperature, T_g. Fourier transform infrared dichroism experiments [12,13] do require a high degree of orientation to achieve sufficient sensitivity but are able to relate measurements to surface orientation or polymer chain relaxations for systems near or above T_g. High SHG signal intensities are observed both above and below T_g as long as there is enough mobility in the matrix for at least a small fraction of the NLO dopants to rotate in response to an imposed electric field. Small changes in dopant rotation can readily be detected as a function of time without causing irreversible change to the matrix or dopant as may occur in a photoisomerization [14–16] or mechanical's experiment. The sensitivity of this optical technique for measuring glassy behavior as a function of temperature is greater than index of refraction experiments [17].

Furthermore beside a variety of approaches, including photon correlation spectroscopy [18] dielectric [19], mechanical[20], NMR [21], fluorescence anisotropy decay [22], excimer probe fluorescence [23], photobleaching [24] that have been used to investigate polymer dynamics, the SHG approach potentially will allow the study of polymer dynamics over a several hundred degree range in temperature. Especially SHG experiment is powerful method to investigate the aging effect [25]. It must be noted that the use of probe molecules to study the dynamics of the surrounding matrix is a delicate matter. The guest molecules must be of proper size and limited amount to perturb the host matrix as less as possible, under the constraint that a good coupling with the matrix must be ensured. The judicious choice of the guest–host system allows one to get quantitative and accurate information on the host via the probe molecules. Examples are provided by photobleaching [24], Electron Spin Resonance [26,27] and SHG [28,29] in conjunction with dielectric relaxation [28,30]. On the other hand, the probe dynamics may decouple from the one of the surrounding matrix, usually resulting in faster motion. This may take place for a number of different reasons, including small molecular size, or the heterogeneous dynamics of the host phase [26,27,31]. However, in fortunate cases the decoupled dynamics of the probe still retains information on the matrix [27].

Our aim is to study structural relaxation of polymers by using the SHG technique. However since the polymer structure is centrosymmetrical, non-linear properties are not present in polymeric systems. To create non-linear response in polymers, we established a guest–host system by adding some probe molecules with large molecular hyperpolarizabilities. Then, by applying electric-field with corona poling on thin samples we could induce polar orientations and this results in noncentrosymmetrical systems that are able to produce a SHG signal. Finally, by removing the electric field the SHG signal drops, which causes the system to relax to a random system.

Measuring the polymer relaxation phenomena by this technique is not straightforward because besides the polymer dynamics, the deposit charge feature in the system also has an effect on average relaxation time [32]. To understand and interpret our data it is essential to take into account the charge effects [33]. So we conducted isothermal poling process above T_g to investigate charge effect on relaxation time. Next, the effect of thermal conditions above T_g on the characteristic time of both the onset and the decay mode was examined. The effect of the poling process on the SHG signal has been widely studied [32–35]. Wang et al. [33–35] found that in a sequence isothermal poling experiment the relaxation time is lengthening after every poling process. It must be pointed out that in most works on SHG, e.g. see [33–35], very limited attention was paid to the SHG onset, most probably due to both experimental complications [28] and the theoretical conclusion [36], with experimental support [28], that the onset and the decay curves exhibit equal relaxation times.

2. Experimental and data analysis

Slightly entangled poly(methy1 methacrylate)(PMMA, M_w = 15 000, T_g = 85 °C) and Disperse red 1 (DR1; *N*-Ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline) were purchased from Aldrich. Polymer + 5wt% DR1 was dissolved in spectroscopic grade dichloromethane and spin coated onto glass part of ITO. The residued solvent was removed by keeping the samples under vacuum for 12 h at 80 °C. The thermal history of the material was erased by keeping the sample above T_g (T_g + 30 °C) for more than 12 h. The DSC measurements to determine the value of T_g were performed by using a Perkin Elmer DSC7. Both samples (pure PMMA and DR1/PMMA mixture) were first heated at 110 °C and held at this temperature for several minutes to erase the thermal history. After cooling down to 30 °C we performed the final heating up to 160 °C. The scans showed a single glass transition at 85 °C for pure PMMA and 80 °C for DR1/PMMA mixture. All the SHG measurements were carried out above T_g. We note that the present study uses atactic PMMA with much lower molecular weight than other studies [33–35]. The molecular weight dependence on the structural relaxation and the glass transition of atactic PMMA is well documented [37]. Due to the lower T_g value, this allowed us to study the relaxation regimes which are accessed by our equipment at lower temperatures, thus limiting the strong tendency of dopant chromophores to escape from the PMMA film.

We used an Excimer laser(Lambda Physik, Model FL2000) to pump a Dye laser(FL-2000). Lasing wavelength is 710 nm, then neither the wavelength of the laser nor the SHG wavelength are located in the absorption peak of the sample. For the detection a photomultiplier(9484 EMI) was used with response of the standard S11 and very low dark current (10 nA) even at room temperature. The repetition rate of the laser was 10 Hz.

In this experiment we used corona poling. Corona poling creates an electric field between the metallic needle and the conducting surface (semitransparent ITO) behind the film. The intense field that is generated at the needle tip creates gas ions with the same polarity as the needle, which are accelerated toward and deposited on the film surface, creating a uniform and high-magnitude field across the material. This field is capable of efficiently orienting the NLO dopant. The corona onset and the stability are a function of the atmosphere in the reaction camera and of electrode geometry. The magnitude of the charge density on sample is a function of the strength and polarity of the applied field, time relative to the field application, and the temperature. When the electric field is less than 5 kV/cm the signal was not detectable, but above 5 kV/cm the signal increased and reaching a constant value over 6.4 kV/cm. On the other hand, the film was easily damaged under too strong electric field, and to avoid any problem the applied electric field was limited to 6 kV/cm.

The chamber heating obtained with two flat resistors placed onto the side walls of the cell. On the two other sides (front and back side) there are two windows for incoming and outgoing beam light. To control the temperature, we inserted a thermocouple through a glass tube from the side wall to a position around 1 mm apart from the point of incidence of laser on sample.

The orientation order of the colorants in the polymer is time dependent. For the lowest investigated temperature (T = 85 °C) the SHG approached a constant value for a poling time of about 12 min for higher temperature lower poling time was needed to reach a constant value.

In this work we used two different experimental strategies. The first type was an isothermal poling/relaxation experiment in which