

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

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Abstract

Second harmonic generation (SHG) is used to monitor the reorientation a dopant chromophore in slightly entangled poly(methyl 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 nonlinear 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, 2, 3, 4]. The interest in using polymers for second-order nonlinear 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, 6, 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, 12, 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 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, 15, 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, nonlinear properties are not present in polymeric systems. To create nonlinear 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 [32,33,34,35]. Wang et. Al. [33,34,35] 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 [33,34,35], 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(methyl methacrylate)(PMMA, $M_w=15000$, $T_g=85^\circ\text{C}$) 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 hours at 80°C . The thermal history of the material was erased by keeping the sample above T_g ($T_g+30^\circ\text{C}$) for more than 12 hours. **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 [33,34,35]. **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 (10nA) even at room temperature. The repetition rate of the laser was 10Hz.

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 6.4kV/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 1mm 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 ($T=85^{\circ}\text{C}$) the SHG approached a constant value for a poling time of about 12 minute 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 the amount of elapsed time between poling cycles was the parameter of interest. Here the sample was poled by applying a large voltage across the ITO electrodes. The SHG signal was monitored and once it had reached a steady state, plateau level, the voltage was removed. The SHG signal was then monitored as it decayed away due to chromophore reorientation. After the SHG signal decayed to an undetectable level, time was allowed to elapse and the process was repeated under identical experimental conditions (i.e. temperature, poling duration, maximum applied poling voltage).

Then for later reason we conducted a second set of isothermal poling experiments after keeping the sample for two hours at 110°C .

To investigate temperature dependence of relaxation time we used a second experimental protocol. First the sample was kept at 110°C then it was cooled down to the measuring temperature. After stabilizing the temperature the electric field was applied to the sample for around 12 min then it was removed and the SHG temporal behaviour was monitored.

Figures 1 & 2 plot the time evolution of the onset and of the decay of the SHG signal for a sample temperature of 85°C. The onset data in fig. 1 are fitted by equation 1,

$$\chi^{(2)}(t) = B - \chi_0^{(2)} e^{-\left(\frac{t}{\tau}\right)} \quad (1)$$

Where B and $\chi_0^{(2)}$ are the background signal and the maximum of second-order macroscopic susceptibility, respectively.

The SHG signal relaxation curve fig. 2 is fitted with the aid of the Kohlrausch-Williams-Watts (KWW) stretched exponential function, of the form

$$\chi^{(2)}(t) = \chi_0^{(2)} e^{-\left(\frac{t}{\tau}\right)^\beta} \quad (2)$$

The KWW function describes the decay processes that have a continuous distribution of relaxation time constants. The parameter β , where $0 \leq \beta \leq 1$, measures the width of the distribution function. A smaller β value corresponds to a broader distribution of relaxation time constants.

To find the temperature dependence of the relaxation processes, the average relaxation lifetime $\langle \tau \rangle$ was calculated by

$$\langle \tau \rangle = \int_0^\infty \exp \left[-\left(\frac{t}{\tau}\right)^\beta \right] dt = \frac{\tau}{\beta} \Gamma \left(\frac{1}{\beta} \right) \quad (3)$$

where Γ is the gamma function.

3) Results and discussion

3.1) Charge effect

Corona poling creates an electric field by generating a discharge from a metallic point source and place a ground electrode behind the film [38,39,40,41]. The electric field gradient created by the corona discharge is due to the ions deposited on the surface, and to a smaller extent to the carriers inherent in the material (space charges)[42]. The magnitude of the charge density is a function of the strength and polarity of the applied field, time relative to

the field application, and temperature [38, 39, 43]. The corona onset and stability are functions of the atmospheric conditions and the electrode geometry.

In particular, we are interested in the effect that the injected charge has on the relaxation rate of the SHG signal induced by the electric poling field. The effect of injected charge was investigated by isothermal experiment.

Results of four different waiting times (between any isothermal experiments) for the decay mode are tabulated in Table 1 and plotted in fig. 3. The stretching parameter for all the isothermal experiments was $\beta = 0.56 \pm 0.03$. It is clear from fig.3, that the first four isothermal polings show evidence of a "memory" effect in which the SHG signal takes progressively more time to decay after each poling. It is our hypothesis that the injected charge is responsible for this effect.

In principle, a possible cause for the increase of the relaxation time τ for the decay mode could be physical aging. Physical aging, is a process where a polymer at or below T_g spontaneously loses free volume when it approaches thermodynamic equilibrium [44]. As the sample is well above T_g , the increasing relaxation time cannot be ascribed to the physical aging. This was also explicitly checked by comparing isothermal poling experiments with different aging times.

After the first four relaxations were performed, the sample was subjected to the thermal erasure procedure described above. The sample was finally exposed to two poling/relaxation cycles (numbers 5 and 6) using the same parameters (temperature, poling field, duration of poling) as the first four ones. One notes that the decay of the SHG signal in experiment 5 exhibits an average relaxation time $\langle \tau \rangle = 247.9\text{s}$ which is not identical to that of experiment 1 (see Table 1), instead, it is closer to experiment 2. The relaxation time of the decay of the 6th cycle, $\langle \tau \rangle = 416.2\text{s}$, is very close to the 3rd one (see Table 1), which demonstrates that after the first poling the system behaves similar for both poling processes.

Our results are in agreement with previous results [33, 34, 35]. Charge injected by the electrodes into the matrix could be responsible for the memory effect in a number of ways. The charge injected and trapped near the surface of the polymer film would create an electric field inside the polymer, which would orient the dipoles in the same direction as the poling field. Charge in the bulk of the polymer would correlate the motion of the chromophore dipoles. This correlation can be understood as follows: Since the effect of the poling field is to orient the NLO molecules so that their dipole moments point in the same direction, this would lead to unfavorable electrostatic interactions between neighboring chromophores. The

presence of an appropriate charge between two chromophores would counteract this interaction. In addition, the presence of such a charge would force a chromophore-charge-chromophore system to behave as a unit. The combined mass and volume of such a unit would be much greater than a single chromophore, thus hindering reorientation. As more and more charge is injected during the subsequent polings, this charge injection scenario predicts that the SHG signal relaxation time will continue to increase until the polymer becomes saturated with charge, after which the relaxation time should remain constant as long as the charge saturation is maintained and no other mechanisms are present.

Now we discuss the onset part of the signal. It was shown that the onset curve is related to $\langle \cos \theta \rangle$ (θ is the angle by the dipole moment between the applied dc field and the dipole moment) [36], a quantity which is also involved in dielectric spectroscopy [45, 46]. Results of four different waiting times (between any isothermal experiments) for the onset mode are plotted in fig. 4, according to the best-fit results by using Eq.1. The direct comparison with the decay times in Fig.3 evidences that, contrary to the theoretical expectations, the decay and the onset times are different. For the onset mode there is no wide difference between the four relaxation times collected at different waiting times, i.e. the "memory" effect of the onset mode is much weaker than the one of the decay mode. It is evident that the onset part of signal is only weakly affected by the deposit charge of the corona poling.

3.2) Temperature effect

We studied the temperature dependence of the SHG relaxation curves as well as the relation between the latter and the polymer dynamics. Over the range of temperatures considered in this study, both the decay and the onset relaxation times were found to decrease monotonically with increasing temperature. This indicates that at higher temperatures, the dipoles have higher mobility due to enhanced free volume and thermal energy. **The influence of the thermal energy and the density on the polymer relaxation has been widely investigated [47,48,49,50,51].**

The stretching parameter β of the decay curve decreases with increasing temperature, i.e. the distribution of relaxation times narrows. We found that stretching changes from $\beta = 0.71$ at $T = 95^\circ\text{C}$ to $\beta = 0.50$ at $T = 85^\circ\text{C}$, in close analogy with previous results [28,52]. **We notice that, due to the poor entanglement of the PMMA chains of our sample, the Rouse theory, predicting $\beta = 0.5$, applies [53].** Any conformational changes require activation energy ΔE_{act} , which is related to $\langle \tau \rangle$ through the following equation [54]

$$\ln\langle\tau\rangle = C + \frac{\Delta E_{act}}{KT} \quad (4)$$

Where C is a constant. The Arrhenius plot of the average relaxation lifetime of the decay mode in Fig. 5 shows that the process is indeed activated. **At first sight this is surprising in that the α -relaxation of PMMA is highly non-Arrhenius [55]. Nonetheless, the consideration of small temperature ranges favours the “linearization” in the Arrhenius plot. This was done in the past close to Tg for *pure* PMMA leading to apparent activation energies of about 450-1000 kJ/mol [19]. Indeed, we considered more recent data [55] and found about 1000 kJ/mol. However, in DR1-PMMA *mixtures* dielectric measurements reveal that the relaxation of PMMA is virtually Arrhenius over the range 80-145 °C for the same DR1 concentration of the present work (5%) and higher ones (see Fig.8 of [56]). In particular, for PMMA with 5% DR1 the activation energy of the main relaxation of PMMA is about 290 kJ/mol (see Table II of ref.[56]). This compares quite well with the activation energy of the decay of our SHG signal (311 kJ/mol) and points to a good coupling between the decay time scale and the structural relaxation time. The conclusion is reinforced by the following two facts:**

- 1) **if the charge memory effects are erased, the average decay time $\langle\tau\rangle$ is about 200 s close to Tg (see Table I of our paper), as expected by the conventional definition of Tg via $\tau_{\alpha}(Tg) = 100$ s;**
- 2) **the decay is stretched with $\beta = 0.5$ close to Tg. Close to Tg ellipsometric measurements on a mixture of DR1 with PMMA of the same molecular weight of the present study yields $\beta = 0.45$ for the α -relaxation, after corrections due to the influence of the β -relaxation [57]. The coincidence of the stretching of the SHG decay and the main relaxation ($\beta = 0.5$) has been also found for DR1 in Poly(isobuty1 methacrylate) [28].**

Fig.6 shows the Arrhenius plot of the characteristic relaxation time of the onset mode. Again, we find an activated behaviour. However, the activation energy is much lower than the one of the decay mode which, in turn, is quite close to the one of the main relaxation of PMMA [56]. **This points to a decoupling of the onset mode by the structural relaxation, a conclusion which is reinforced by the finding that the time-dependence of the SHG onset is exponential and not stretched (see Fig. 1). Also, notice that the comparison of Figs. 3 and 4 as well as Figs. 5 and 6 shows that the onset is faster than the decay. We tentatively ascribe this facilitated dynamics to the poling field, which, owing to the**

limited laser power, is quite high. Due to the inherently homogeneous character of the torque imposed by the poling field, the virtual absence of stretching (basically due to heterogeneities) of the onset mode is anticipated. We also notice that the influence of the surface charge and the charge memory effect results in the increase of the decay relaxation time of a factor of three after four poling cycles (see Fig.3). This is less than the factor of seven of the ratio between the (slow) decay and the (fast) onset characteristic times if charge effects are erased (compare the points with zero waiting times in Figs. 3 and 4). This suggests that the acceleration effect of the poling field on the onset mode with respect to the decay mode is more important than the slowing down due to the presence of the charges. This argument may explain the weak evidence of charge memory effect in the onset mode.

4) Summary

In situ SHG is sensitive for probing amorphous polymer physics at different temperatures. When the field is applied, the SHG intensity and $\chi^{(2)}$ increase as dopants in the regions of sufficient mobility and local free volume align in the field direction. This dynamical process was poorly considered by previous studies. Dopant disorientation is related to polymer relaxation phenomena and surface charge persistence. The SHG technique is sensitive to small changes in dopant orientation relating to the local microenvironment surrounding the NLO dopants, and the stability of the dopant orientation depends strongly on the microenvironment around the dopant, including segmental mobility and local free volume. We found out that surface and trapped charges in thin films of a guest-host system play an important role. **It was evidenced that, if they are absent, the decay dynamics of the SHG tracks the one of the main relaxation (stretching, time scales and activation energy). Differently, the onset dynamics is faster and exponential, probably due to the influence of the poling field. If surface and trapped charges are more and more present in the film, the onset dynamics is almost unaffected (due to the competing effect of the poling field), whereas the decay dynamics is increasingly slowed down without changing the stretching.**

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Table 1: Relaxation parameters of the decay mode for different waiting time at $T=87.5^{\circ}\text{C}$ of PMMA+5wt%DR1

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- 3) Isothermal experiment for PMMA+5wt%DR1 at T=87.5°C: average relaxation time of the decay mode vs. the waiting time.
- 4) Isothermal experiment for PMMA+5wt%DR1 at T=87.5°C: average relaxation time of the onset mode vs. the waiting time.
- 5) Arrhenius plot of the average relaxation time of the decay mode for PMMA+5wt%DR1.
- 6) Arrhenius plot of the average relaxation time of the onset mode for PMMA+5wt%DR1.

Table

	Waiting time t_w(min)	\bar{t}(s)	$\langle \bar{t} \rangle$(s)
1	0	121.8	191.8
2	97	173.4	279.9
3	172	219.1	395.7
4	267	330.5	547.5

Table 1

Figures

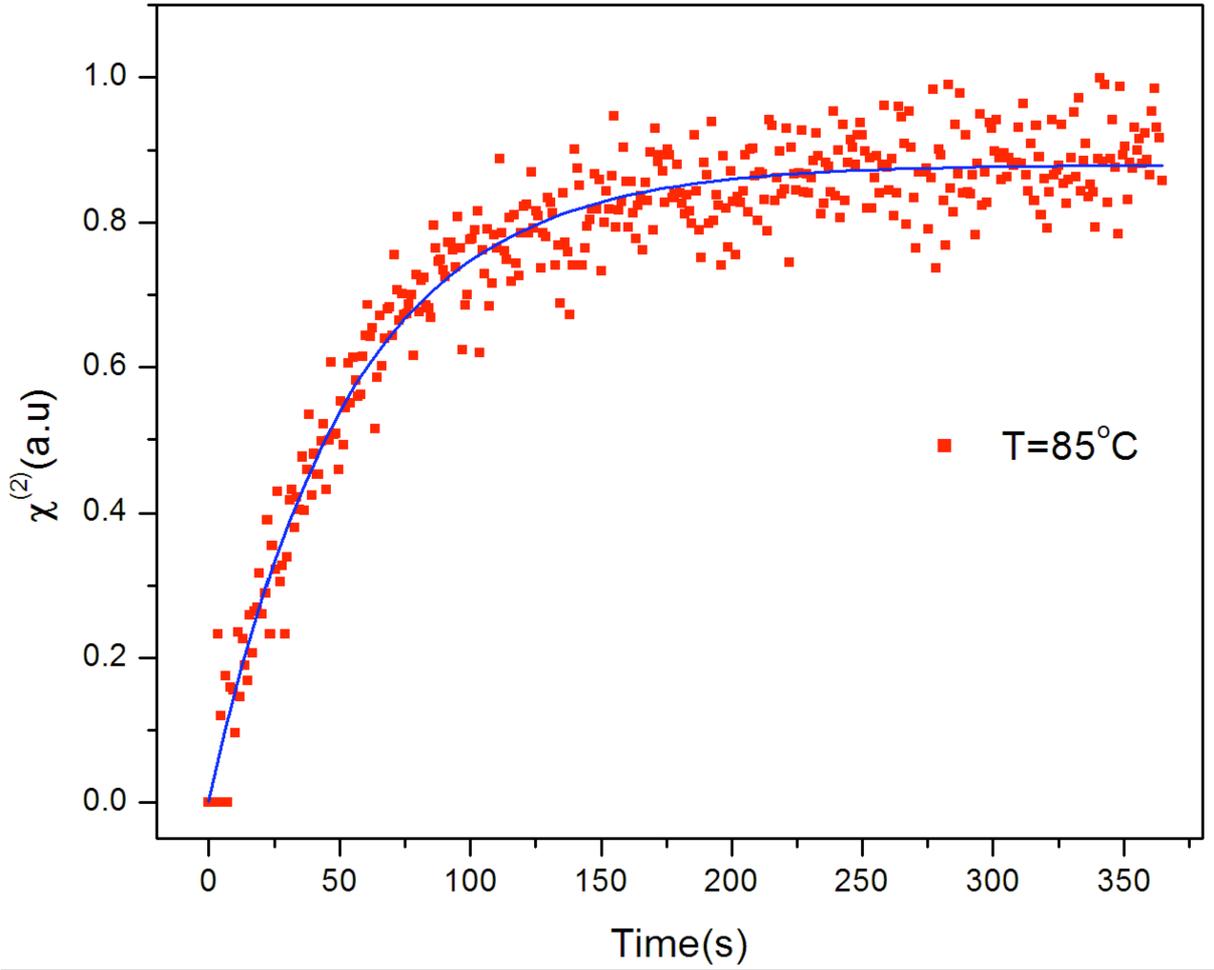


Figure 1.

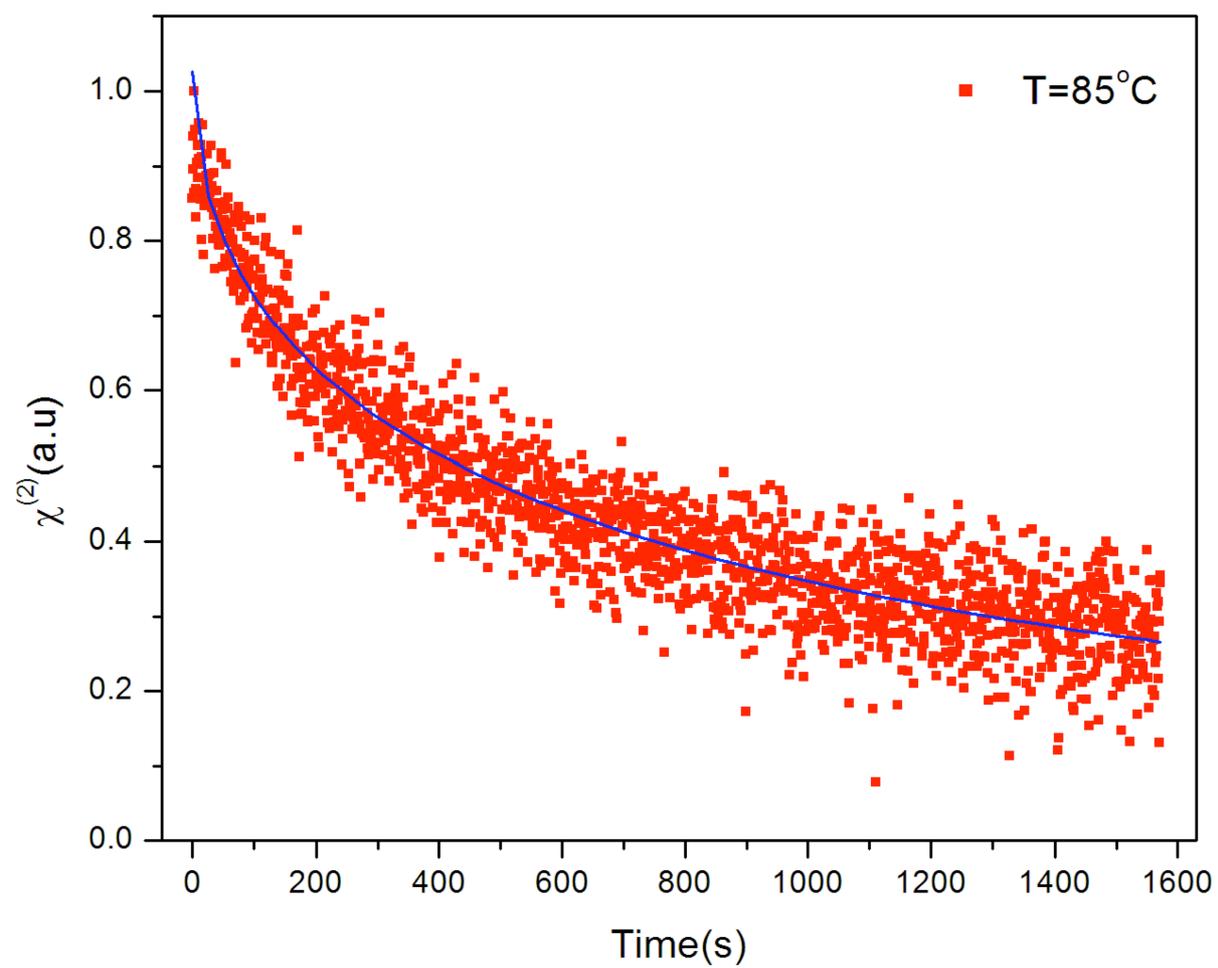


Figure 2

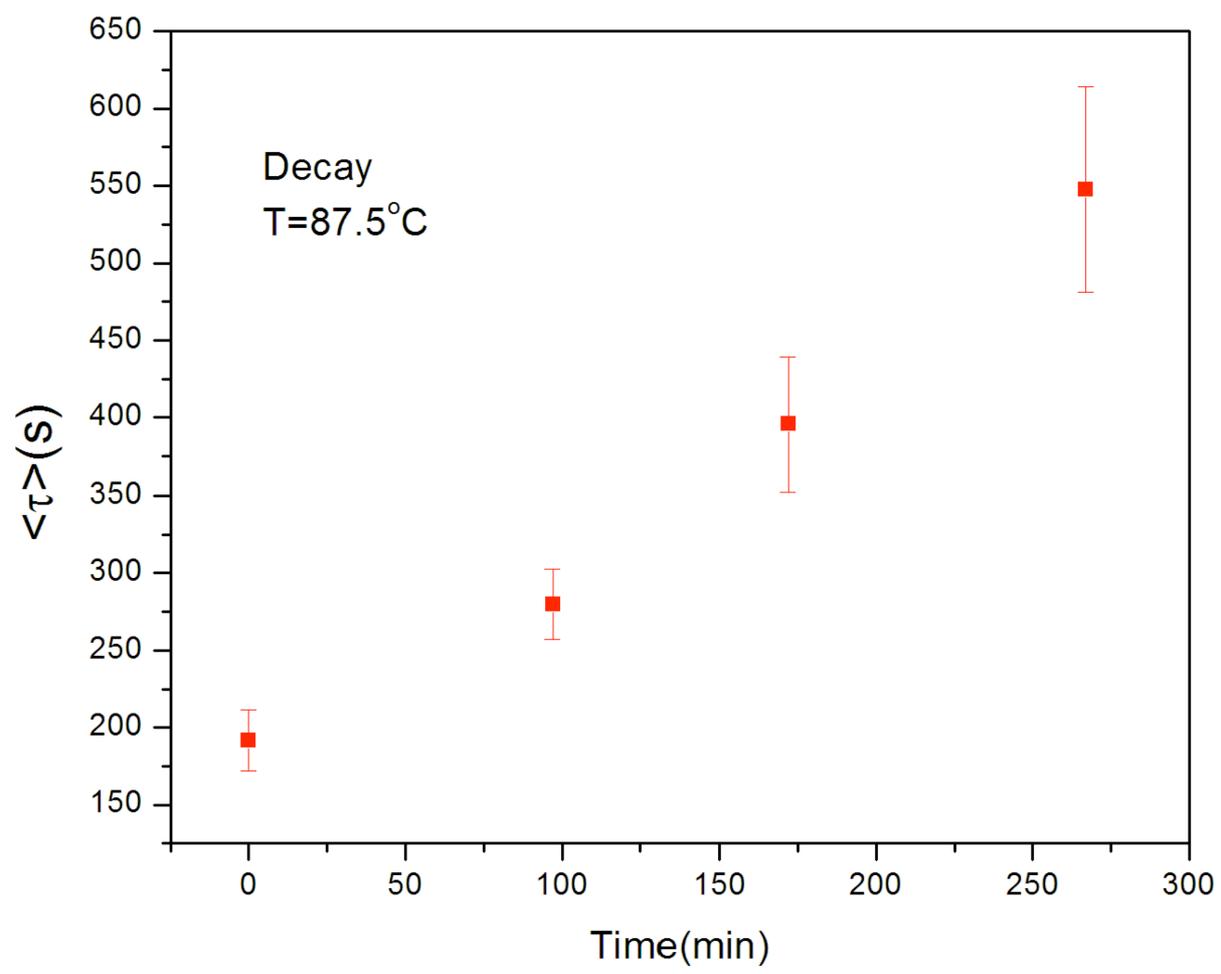


Figure 3

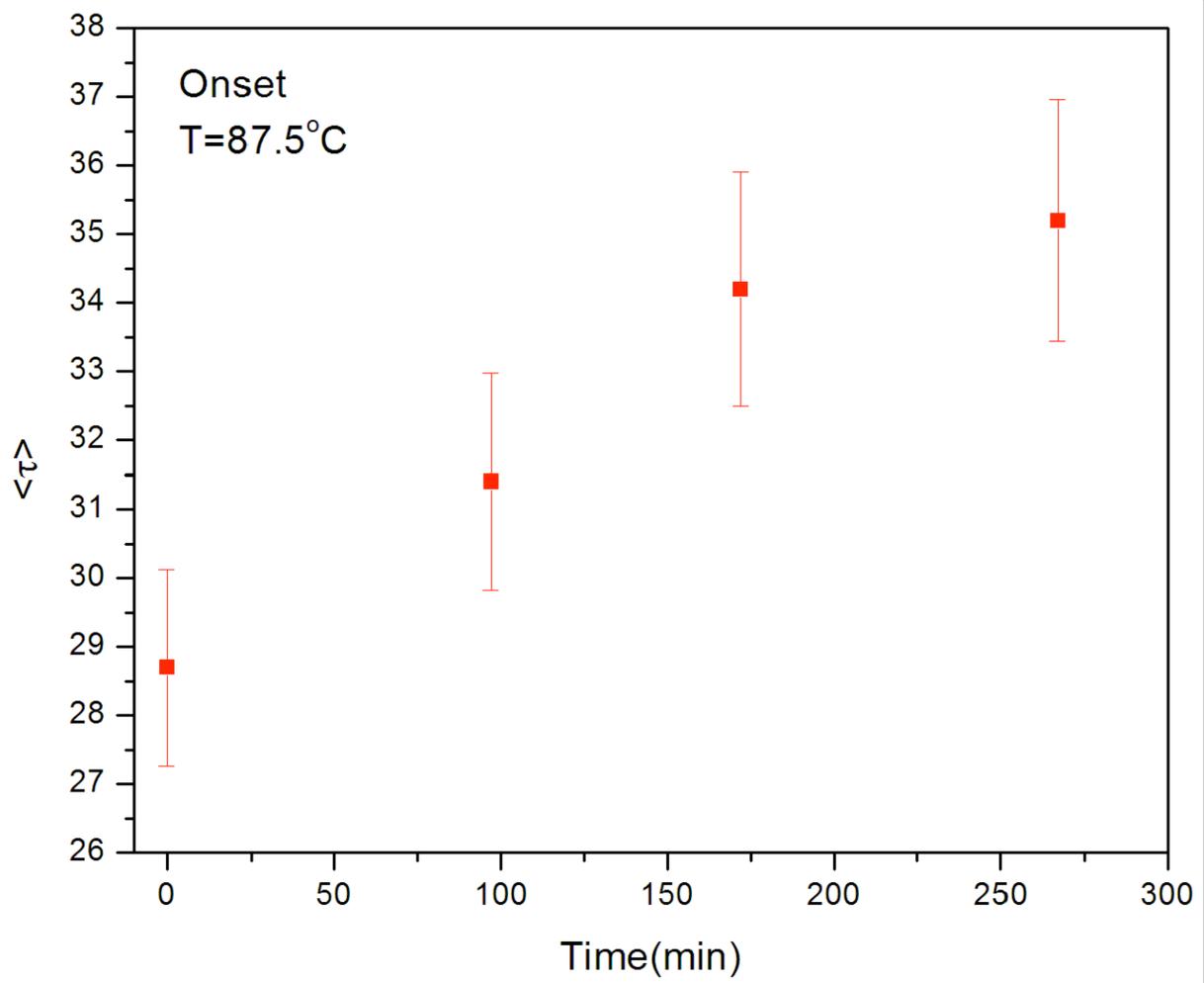


Figure 4

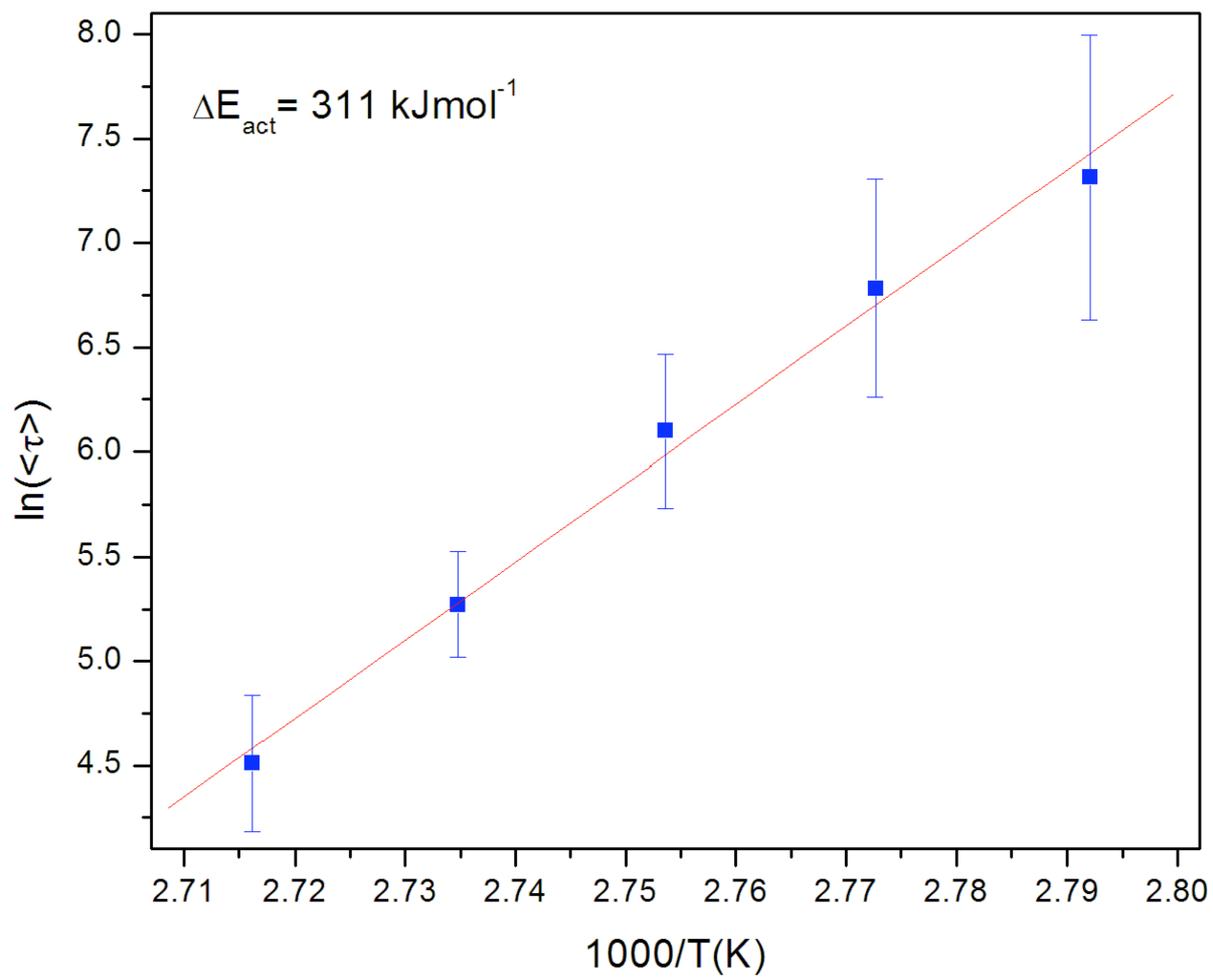


Figure 5

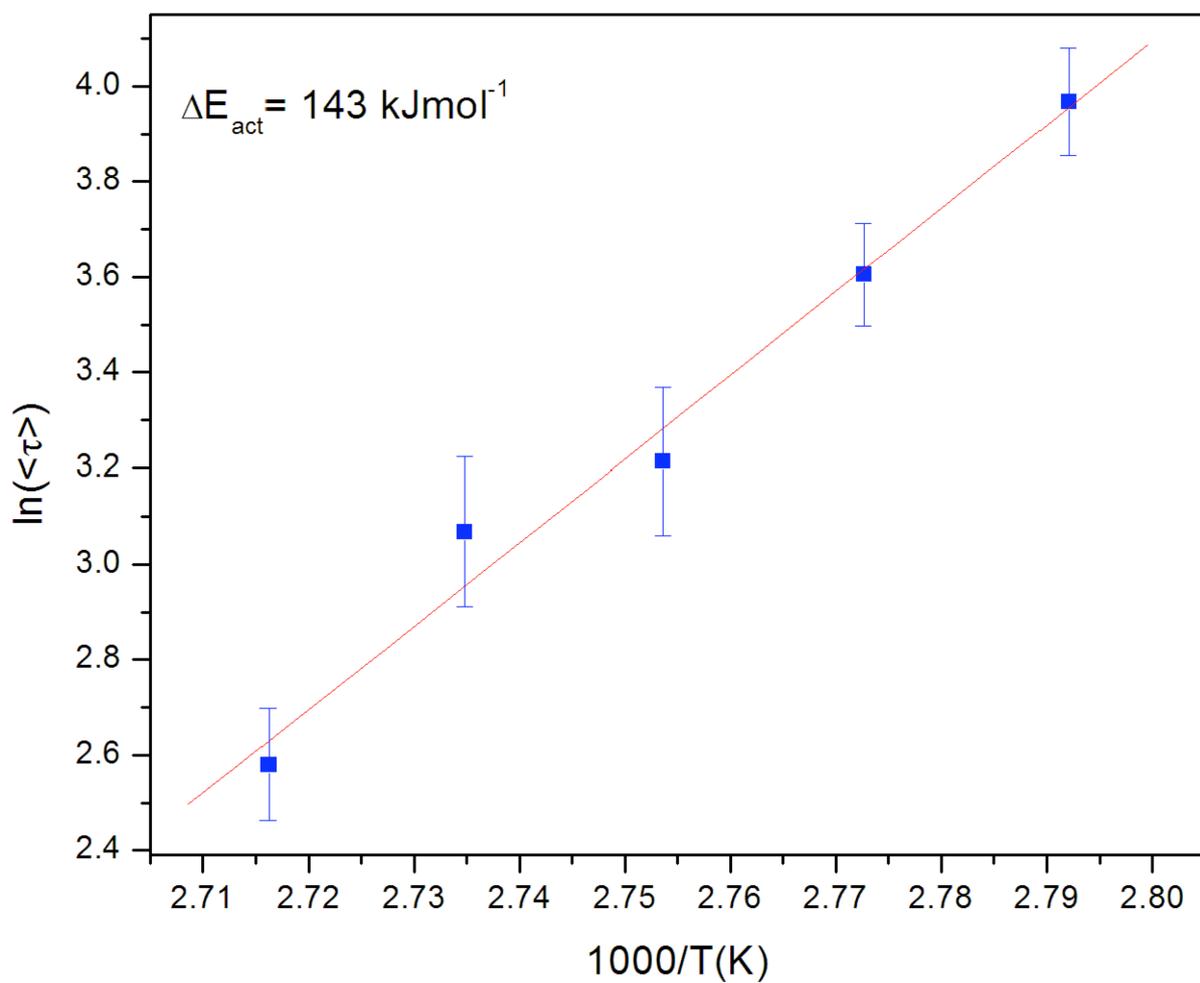


Figure 6