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Determination of Activation Energy for the Number Average Degree of Polymerization Using the Fluorescence Method

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A novel method based on steady state fluorescence measurements is introduced for measuring the activation energy of the number average degree of polymerization (NADP). Pyrene (Py) was used as a fluorescence probe for real time monitoring of free-radical polymerization (FRP) of methyl methacrylate (MMA). *In situ* FRP experiments were performed at various temperatures. Positive activation energy for NADP was measured and found to be 9.2 kcal/mol.

Introduction

Steady state fluorescence spectra of many chromophores are sensitive to the polarity of their environment. The interactions between the chromophore and the solvent molecules effect the energy difference between the ground and the excited states. This energy difference is called the Stokes shift, and depends on the refractive index and dielectric constant of the solvent. Recently, by measuring the Stokes shift of a polarity sensitive fluorescence molecule, the gelation during epoxy curing was monitored as a function of cure time[1]. Time-resolved and steady-state fluorescence techniques wer employed to study isotactic polystyrene in its gel state. Excimer spectra were used to monitor the existence of two different conformations in the gel state of polystyrene. Pyrene derivative was used as a fluorescence molecule to monitor the polymerization, aging and drying of aluminosilicate gels[2]. These results were interpreted in terms of the chemical changes occuring during the sol-gel process and the interactions betweenthe chromophores and the sol-gel matrix. Recently, we reported in situ observations of the sol-gel phase transition in free-radical crosslinking copolymerization using the fluorescence technique[3–5].

In this paper we use quenching properties of the excited state of a fluorescing molecule to study the free radical polymerization of methyl methacrylate (MMA). Pyrene (Py) is used as a fluorescence probe for the *in situ* polymerization experiments. Number average degree of polymerization ($\bar{X}_n$) was measured at different temperatures and its activation energy, ΔE_x was calculated. In order to interpret the data an empirical relation for the Py intensity is introduced for a given temperature.

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Fluorescence Medhod

Fluorescence and phosphorescence intensities of aromatic molecules are affected by both radiative and non-radiative processes[6]. If the possibility of perturbation due to oxygen is excluded, the radiative probabilities are found to be relatively independent of environment and even of molecular species. Environmental effects on non-radiative transitions which are primarily intramolecular in nature are believed to arise from a breakdown of the Born-Oppenheimer approximation[7]. THe role of the solvent in such a picture is to add the quasi-continuum of states needed to satisfy energy resonance conditions. The solvent acts as an energy sink for rapid vibrational relaxation which occurs after the rate limiting transition from the initial state.

Years ago, Birks *el. al* studied the influence of solvent viscosity on fluorescence characteristics of pyrene solutions in various solvents and observed that the rate of monomer internal quenching is affected by solvent quality[8]. Weber et al reported the solvent dependence of energy trapping in phenanthrene block polymers and explained the decrease in fluorescence yield with the static quenching, caused by the solvent induced trapping states[9]. As the temperature of liquid solution is varied, the environment about the molecule changes and much of the change in absorption spectra and fluorescence yields in solution can be related to the changes in solvent viscosity. A matrix than changes little with temperature will enable one to study molecular properties themselves without changing environmental influence. Poly (methyl methacrylate) (PMMA) has been used as a matrix in many studies[10]. Recently we have reported viscosity effects on low frequency, intramolecular vibrational energies of excited naphthalene in swollen PMMA latex particles[11].

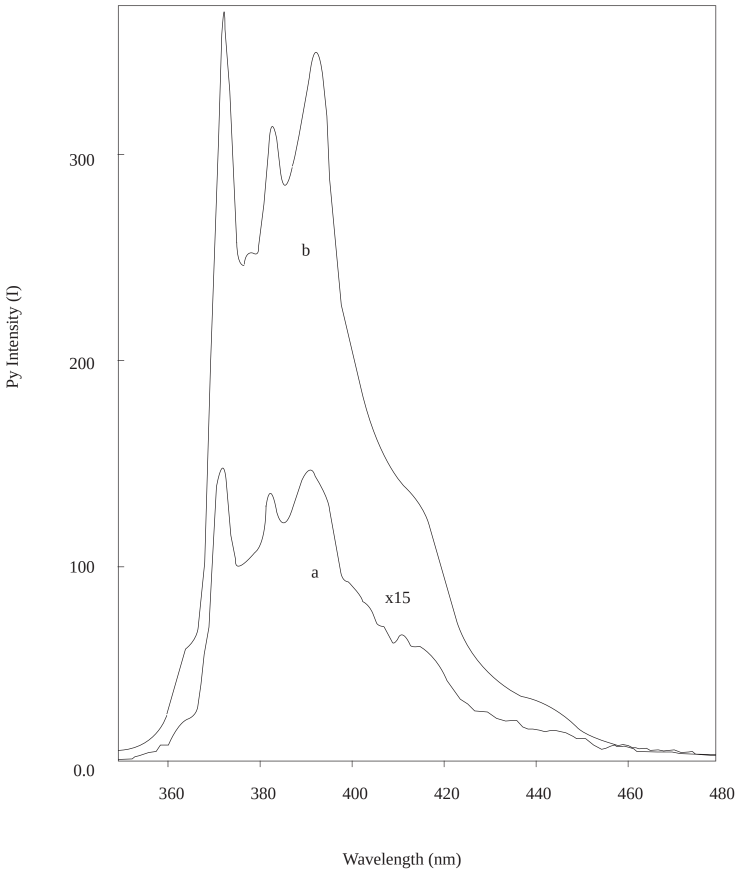

Figure 1. A typical fluorescence emission spectra of Py a- before, b- after the free radical polymerization (FRP). Py molecules are excited at 345 nm.

Experimental

In this work we monitored the free radical polymerization (FRP) of MMA by using by using in situ steady-state fluorescence technique. The FRP processes were performed separately at 65, 70, 75, 80 and 85° C temperatures and monitored against reaction time, t. The radical copolymerization of MMA was performed in bulk in the presence of 2,2′-azobisisobutyronitrile (AIBN) as an initiator. Py was used as a fluorescence probe to detect the FRP process, where MMA and linear poly(methyl methacrylate) PMMA chains act as energy sinks for the excited Py during polymerization. Later, the formation of bulk PMMA provides an ideal, unchanged environment for the excited Py molecules. Naturally, from these experiments one may expect a substantial increase in fluorescence intensity, I, of Py at certain time intervals.

In situ steady-state fluorescence measurements were carried out using the Model LS-50 spectrofluorimeter (Perkin Elmer) equipped with temperature controller. All measurements were made at 90° position and slit widths were kept at 2.5 mm.

The monomer MMA (Merck) was freed from the inhibitor by shaking with a 10% aqueous KOH solution, washing with water and drying over sodium sulfate. Monomer was then distilled under reduced pressure over copper chloride. The initiator, AIBN (Merck), was recrystallized twice from methanol was used during FRP processes.

AIBN (0.26 wt%) was dissolved in MMA and this stock solution was divided and transferred into round glass tubes of 15 mm internal diameter for fluorescence measurements. Six different samples were prepared for the fluorescence experiments. All samples were deoxygenated by bubbling nitrogen through reaction mixtures for 10 minutes. Radical copolymerization of MMA was performed at 60, 70, 75, 80 and 85° C, in the fluorescence accessory of spectrofluorimeter.

Results and Discussion

Py molecule was excited at 345 nm during *in situ* experiments and variation in fluorescence emission intensity, I, was monitored with the time-drive mode of the spectrometer, by staying at the 395 nm peak of the Py spectra. Typical Py spectra are shown in Figure 1 before and after polymerization. No shift was observed in the wavelength of the maximum intensity of Py and all samples have kept their transparency during polymerization process. Normalized Py intensities, I versus reaction times are plotted in Figure 2 for samples polymerized at elevated temperatures. In Figure 2 it is seen that all curves show sudden increase at different temperatures, and then reach equilibrium. At lower temperatures the increase in I takes place at longer times indicating that polymerization is slower at low temperatures.

In order to quantify the above results and empirical relation is introduced by assuming that Py intensity, I increases as polymerization propagates. In order words as monomer consumption increase due to polymerization, Py molecules are being trapped in the rigid PMMA environment, as a result I increases. Intuitively the following relation can be written by assuming that I monitors the polymerization for a given temperature

$$I = I_\infty [1 - exp(-\bar{X}_n \alpha (t - t_0))] \tag{1}$$

here I_∞ presents the Py intensity at $t = \infty$ where all the monomer has polymerized. $\bar{X}_n$ is the number average degree of polymerization which is given by the following relation[12].

$$\bar{X}_n = \bar{X}_{no} exp(\Delta E_x / kT) \tag{2}$$

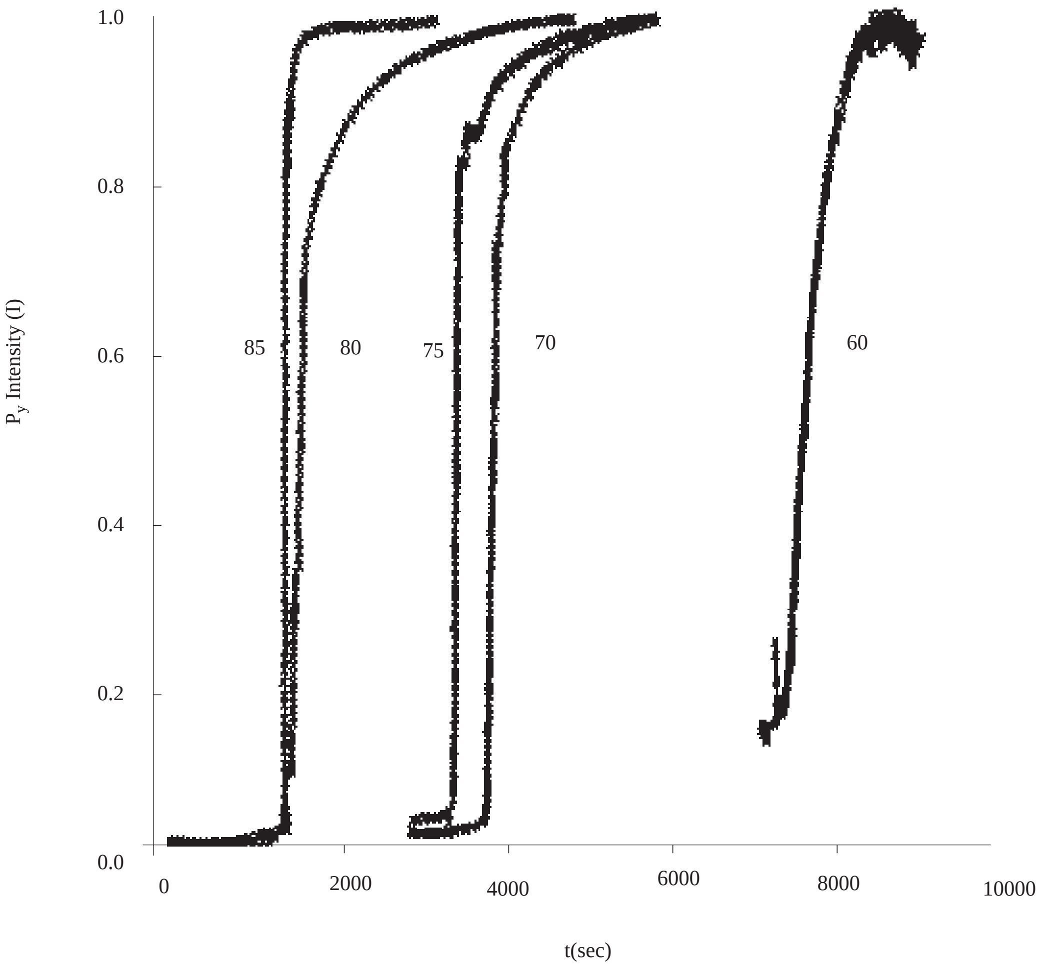

Figure 2. Plots of Py fluorescence intensity, I against reaction time, t during FRP. Time drive mode of the spectrometer was employed and the maximum intensity peak at 395nm polymerization temperature in °C.

where

$$\Delta E_x = \Delta E_i/2 + \Delta E_t/2 - \Delta E_p \tag{3}$$

is the total activation energy for $\bar{X}_n$, k is the Boltzmann constant and T is the temperature. Here ΔE_i, ΔE_p and ΔE_k are the initiation, propagation and termination activation energies and can be given by the corresponding rate constants as follow[12].

$$k_i = A_i exp(-\Delta E_i/kT) \tag{4a}$$

$$k_p = A_p exp(-\Delta E_p/kT) \tag{4b}$$

$$k_t = A_t exp(-\Delta E_t/kT) \tag{4c}$$

In fact $\bar{X}_n$ and $\bar{X}_n$ are composed of k_i, k_p and k_t rates. Here A_i, A_p and A_t are temperature independent factors. In general ΔE_x is positive and so an increase in temperature, T leads to a reduction in $\bar{X}_n$ although the rate of polymerization continues to increase. In Eq (1) t_0 is chosen so that the following conditions are satisfied;

$$\begin{aligned} I &= 0 \quad at \quad t = 0 \\ I &= I_\infty \quad at \quad t = t_\infty \end{aligned} \tag{5}$$

In summary, for a given temperature and t_0, Eq (1) produces the relation for the chain propagation and provides us with $\bar{X}_n$ parameter. In Eq (1), α is the proportionality constant which takes care of the unit in the exponent.

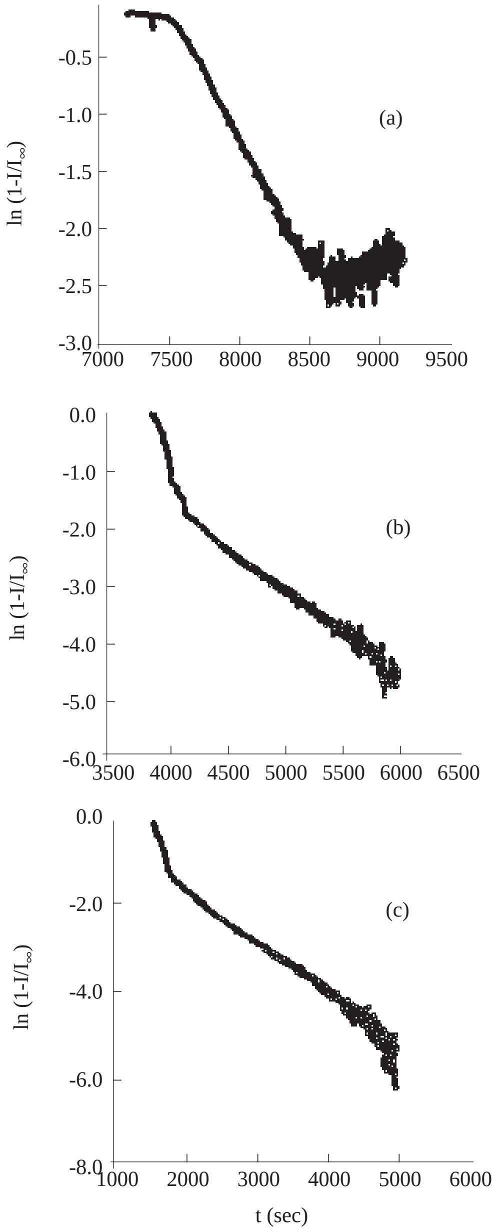

Figure 3. Plots of the digitized data in Fig 2, Which obey Eq(6). a, b and c present the data for samples polymerized at 60, 70 and 80 °C temperatures respectively.

The digitized Py intensities versus reaction times, t are plotted in Fig 3a, b and c according to the logarithmic form of Eq (1) as

$$ln(1 - I/I_\infty) = -\alpha \bar{X}_n (t - t_c) \tag{6}$$

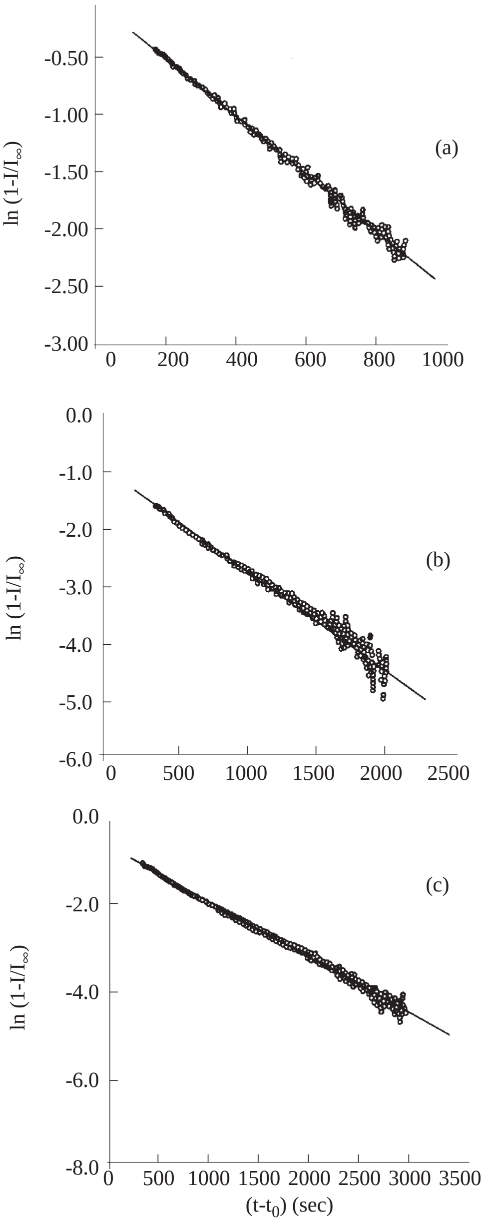

Figure 4. Comparison of the linear partions of the data presented in Fig 3a, b and c which the computations using Eq (6). Number averaged degree of polymerization, $\bar{X}_n$ parameters were obtained from the slopes of plots in a, b and c for 60, 70 and 80 ° respectively. Here, t_0 is chosen, so that it presents the beginning of the linear portion of the curve.

for the samples polymerized at 60, 70, 80 °C, respectively. Except at early times, curves in Fig3a, b and c present nice linear relations. When the linear portions of the curves in Fig 3 are compared to computations using Eq (6), $\bar{X}_n$ parameters are produced from the slopes f the curves (See Fig 4). THe obtained $\bar{X}_n$

parameters are plotted versus temperature in Fig 5. As predicted, $\bar{X}_n$ values decrease as temperature, T is increased. THis behavior can be explained with Eq (2) for the positive ΔE_x activation energy. Logarithm of $\bar{X}_n$ parameters are plotted versus T^{-1} in Fig 6, where ΔE_x=9.2 kcal/mol is obtained from the slope of the strait line. The positive activation energy (ΔE_x) for NADP was already calculated in the literature[12] for benzoyl peroxide and MMA for ΔE_i=29.66 kcal/mol, ΔE_p=4.78 kcal/mol and ΔE_x=1.19 kcal/mol as 10.64 kcal/mol, which is very close to our finding.

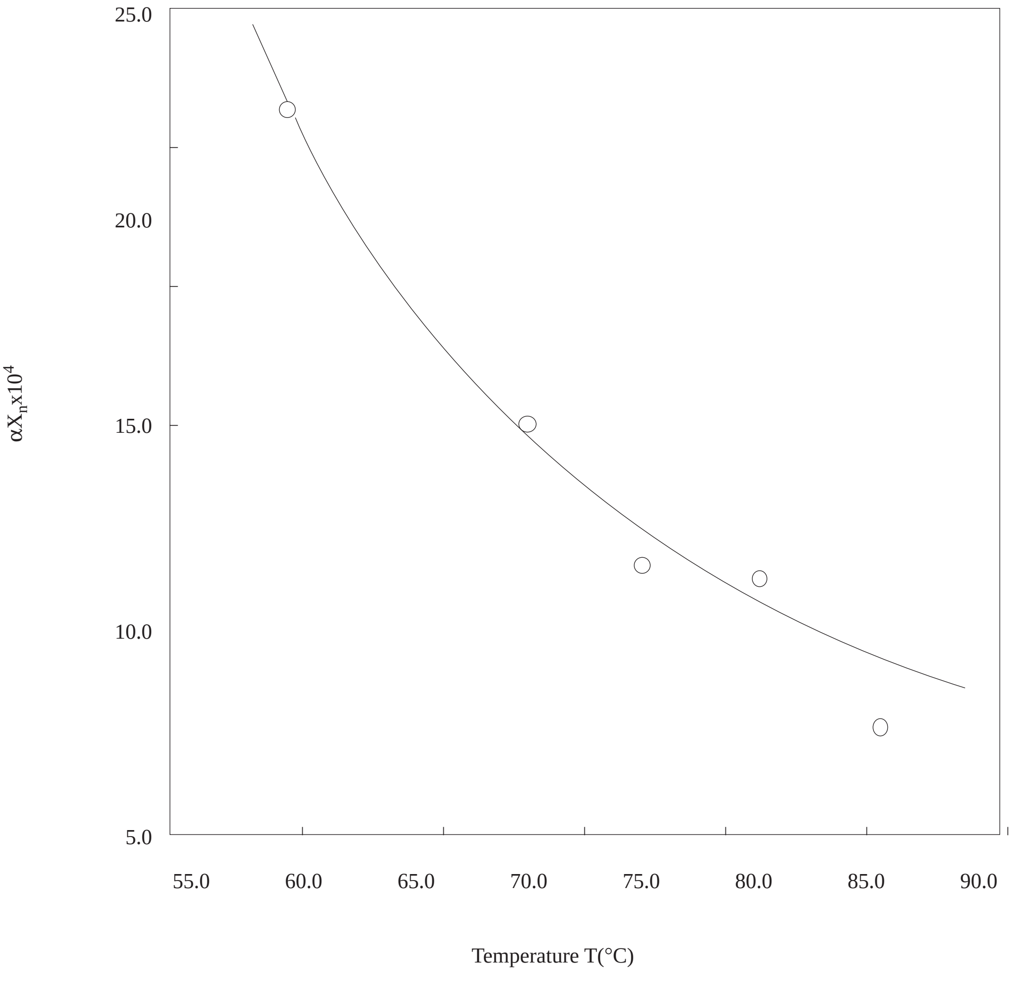

Figure 5. Plot of $\alpha\bar{X}_n$ versus T for the samples polymerized at 60, 70, 75, 80 and 85 °C temperatures.

In conclusion, the aim of this short report is to introduce a novel fluorescence technique to measure the number average degree of polymerization, $\bar{X}_n$ and its corresponding positive activation energy. At this stage of the work a useful empirical relation was used to interpret the time behavior of fluorescence intensity. In future work a proper model has to be derived to convince the reader that this simple, novel technique is really appropriate for measuring FRP parameters.

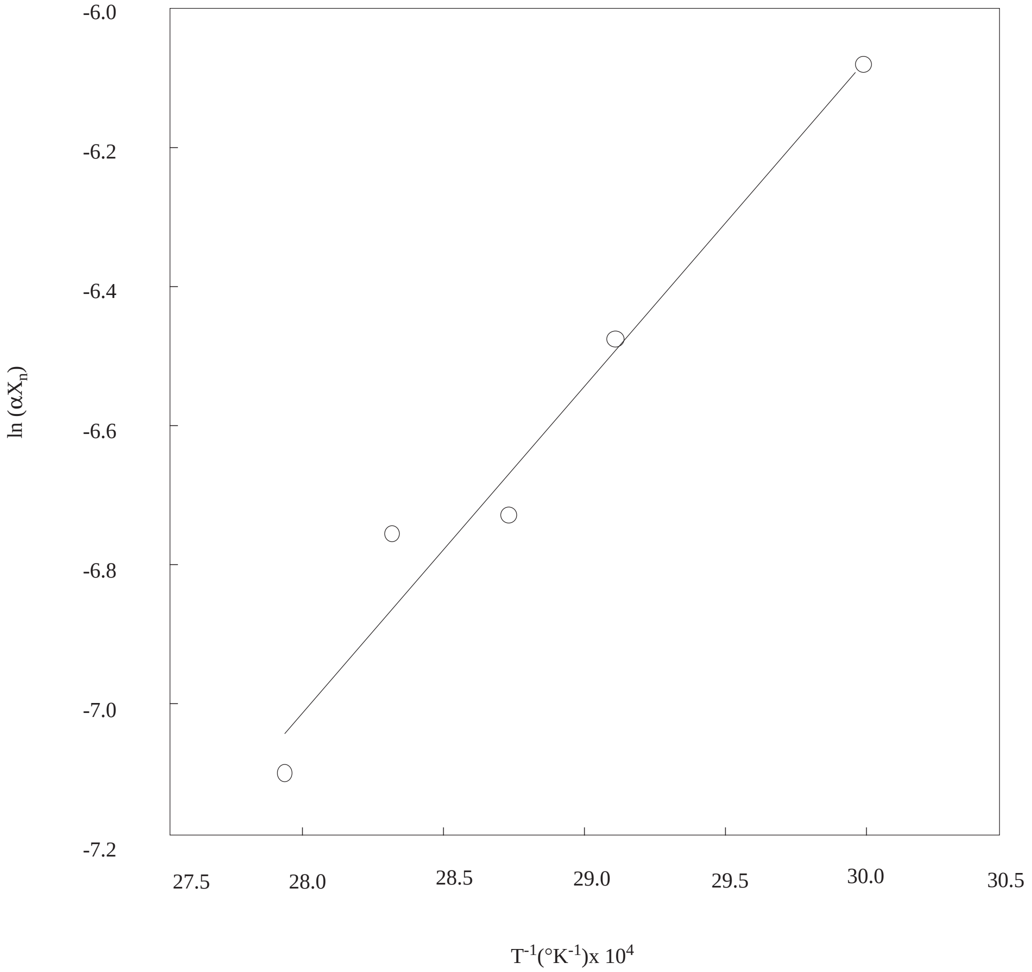

Figure 6. Logarithmic plot of $\bar{X}_n$ versus T^{-1} for the samples polymerized at 60, 70, 75, 80 and 85 $^\circ$C temperatures. ΔE_x is producted from the slope of the plot according to Eq 2.

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