

A DSC Study of α - and β -Relaxations in a PS–Clay System

Sergey Vyazovkin* and Ion Dranca

Department of Chemistry, University of Alabama at Birmingham, 901 S. 14th Street, Birmingham, Alabama 35294

Received: March 23, 2004; In Final Form: June 4, 2004

Differential scanning calorimetry has been used to study the α -relaxation (glass transition) as well as β -relaxation (sub- T_g relaxation) in both virgin polystyrene (PS) and PS–clay nanocomposite. The β -relaxations have been measured as a small endothermic peak that appears on heating of the samples previously annealed at temperatures from 30 to 80 °C. The relaxations have been characterized by determining the effective activation energies (E) and evaluating the sizes of cooperatively rearranging regions at the glass transition (V_g). The values of V_g have been determined from the heat capacity data. The β -relaxation in both systems shows comparable values of E that increase with annealing temperature from ~ 90 to 170 kJ mol^{-1} . In the PS–clay system the increase occurs slower, suggesting that this process is more decoupled from the α -relaxation than in virgin PS. The α -relaxation demonstrates markedly larger values of E (~ 340 vs $\sim 270 \text{ kJ mol}^{-1}$) for the PS–clay system than for virgin PS. The PS–clay system has also been found to have a significantly larger value of V_g , 36.7 nm^3 as compared to 20.9 nm^3 for PS. The increase in E and V_g reflects an increase in molecular cooperativity that is introduced by the mutually dependent motion of the polymer chains anchored to the surface of clay sheets.

Introduction

Differential scanning calorimetry (DSC) is a major tool for measuring the glass transitions or, so-called, α -relaxations in polymer systems.¹ In particular, it has been successfully employed to explore glass transitions in various nanostructured polymer systems, including thin films^{2,3} and polymers confined to nanopores.^{4,5} However, DSC is rarely used for measuring the sub- T_g or β -relaxations because the thermal effects are very small and difficult to detect under regular conditions. Nevertheless, Wunderlich and Bodily⁶ have detected the sub- T_g relaxation in PS at ~ 50 °C when applying the method of differential thermal analysis to samples of a large size (0.5 g). As was originally shown by Illers⁷ for PVC, the sub- T_g peaks can also be revealed for small samples when annealing at temperatures well below T_g . During annealing a glassy polymer relaxes toward equilibrium, therefore losing enthalpy. The lost enthalpy is recovered on successive heating, giving rise to an endothermic peak. The size of this peak is proportional to the enthalpy loss that increases with the time of annealing. Chen and Wang⁸ have been able to reliably detect the sub- T_g peaks in $\sim 7 \text{ mg}$ samples of PS by annealing them from 5 to 260 h. A somewhat different approach has been taken by Bershtein and Egorov,^{9,10} who use very fast cooling rates to reach the glassy state that is farther removed from equilibrium. Because the relaxation rate is proportional to the distance from equilibrium, the enthalpy loss on annealing occurs faster, which allows the annealing times to be reduced to less than 1 h.

Chen and Wang⁸ have suggested that the sub- T_g relaxation may have a common molecular origin with the glass transition and that both can be described by a single relaxation spectrum with a long tail extending toward the short time range. Bershtein and Egorov¹⁰ also suggest a common origin of these two

processes and provide compelling evidence that the sub- T_g relaxation is, in fact, the β -relaxation that had been widely observed by using mechanical and dielectrical spectroscopy. The idea of a common molecular origin of the α - and β -relaxations continues to receive further experimental and theoretical support.^{11–13} Note that Johari and Goldstein¹⁴ have also observed the secondary sub- T_g relaxations in simple inorganic glasses and stressed the striking similarity with the relaxation of polymer glasses. This secondary β -relaxation is frequently referred to as the Johari–Goldstein process.¹⁵ An excellent discussion of the interrelationship between the α - and β -processes is given in the recent book by Donth.¹⁵ There appears to be a growing tendency to interpret the β -process as a primitive relaxation that transforms into the α -relaxation by cooperative slowing down.^{10,13,15,16}

The phenomena leading to sub- T_g peaks have been explained by Kovacs et al.¹⁷ in the framework of the so-called KAHR model of the glass relaxation. The Tool¹⁸–Narayanaswamy¹⁹–Moynihan²⁰ model is also capable of simulating the sub- T_g effects, as was demonstrated by Hodge and Berens.²¹ Although the TNM and KAHR models may give rise to sub- T_g peaks, their quantitative application is limited to a rather narrow temperature region (down to about 20 °C below T_g ²²). Unfortunately, the models have not been successful^{23,24} in describing annealing at temperatures far below T_g .

In this work, we apply DSC to measure the α - and β -relaxations in a PS–clay system as well as in virgin PS. The objective of this study is to obtain comparative information on the relaxation dynamics of these systems by estimating the effective activation energies of the relaxations as well as the sizes of cooperatively rearranging regions at the glass transition. To our knowledge, these parameters have not been reported yet for any polymer–clay systems, although there is a significant body of literature on their thermal properties.

* To whom correspondence should be addressed. E-mail: vyazovkin@uab.edu.

Experimental Part

A sample of the PS–clay composite was provided by Dr. Xiaowu Fan (Northwestern University). The composite was prepared by intercalating a monocationic free radical initiator into montmorillonite clay and the subsequent solution surface-initiated polymerization (SIP), where the chain growth was initiated in situ from clay surfaces. The montmorillonite clay was Cloisite Na⁺ (Southern Clay Product Inc.) with the cation exchange capacity 92 mequiv per 100 g and the specific surface area 750 m² g^{−1}. The initiator was an azobisisobutyronitrile (AIBN)-analogue molecule with a quaternized amine group at one end. The intercalation process was realized by cation exchange reaction in which the cationic end of the initiator was ionically attached to the negatively charged clay surfaces. The details regarding the preparation and characterization of the intercalated clay can be found elsewhere.²⁵ The subsequent SIP was performed in THF solvent with styrene as the monomer, resulting in a PS–clay nanocomposite by the in situ polymerization. Details of the initiator synthesis, the SIP process, and product analysis can be found in a previous publication,²⁶ which shows that this free radical SIP strategy can achieve exfoliated PS–clay nanocomposites of high clay loading. According to our previous TGA measurements,²⁷ the resulting composite contains about 1% of clay by weight. The molecular weight ($\sim 90\,000$) and polydispersity (~ 2.3) of the product were measured by size exclusion chromatography (SEC) using PS standards.²⁷ The obtained material will be referred to as nPS90. For comparison purposes, we have used radically polymerized PS that was purchased from Alfa Aesar and used as received. Its M_w value is 100 000 (polydispersity is around 2.4), and it will be referred to as PS100.

The α -relaxation measurements were performed on ~ 10 mg samples placed in 40 μ L Al pans. The glass transition was measured by heating a sample ~ 40 °C above its glass transition temperature and holding it at this temperature for 10 min to erase thermal history. The samples were then cooled to ~ 40 °C below the glass transition temperature at the rates of 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5, and 25 °C min^{−1}. Immediately after completion of the cooling segment, the samples were heated at a rate whose absolute value was equal to the rate of preceding cooling. The β -relaxation measurements were conducted by quickly heating ~ 20 mg samples to 180 °C (TGA data²⁷ indicate that no detectable degradation of PS100 and nPS90 occurs in air below 240 °C) in a furnace under air and immediately quenching them in liquid nitrogen. The samples were then quickly transferred to DSC, where they were annealed for 30 min at a certain temperature, T_a , below T_g . The annealing temperatures were 30, 40, 50, 60, 65, 70, and 80 °C. After completion of the annealing segment, the samples were cooled to -30 °C and immediately heated above T_g . The heating rates were 5, 7.5, 10, 12.5, 15, and 20 °C min^{−1}. The heat capacity was measured by using a standard procedure that is precise to 1%.¹ A sapphire sample of 41.48 mg was used as the calibrant. The temperature program used for the heat capacity measurement involved 5 min isothermal hold at 40 °C followed by heating at 10 °C min^{−1} to 140 °C and another 5 min isothermal hold at the final temperature. All the aforementioned measurements we conducted by using a Mettler-Toledo heat flux DSC 822e in the atmosphere of nitrogen flow (80 mL min^{−1}). The temperature and heat flow calibration were performed by using an indium standard.

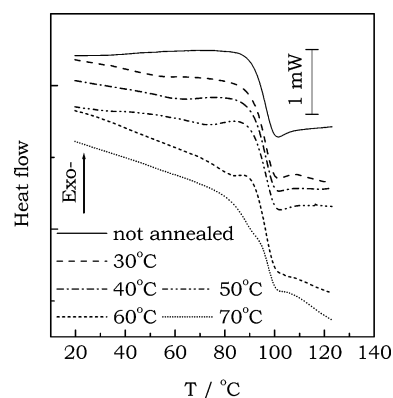


Figure 1. DSC curves obtained on heating of virgin polystyrene (PS100) at 10 °C min^{−1} after annealing at different temperatures.

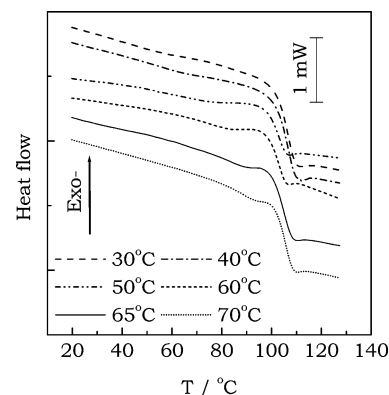


Figure 2. DSC curves obtained on heating polystyrene–clay system (nPS90) at 10 °C min^{−1} after annealing at different temperatures.

Results and Discussion

Sub- T_g or β -Relaxation. Figures 1 and 2 demonstrate evolution of the sub- T_g peaks with the annealing temperature. The DSC curve related to the nonannealed PS sample shows (Figure 1) a small exothermic event that is typically observed for glassy systems that are heated at a slower rate than the rate of preceding cooling.¹ This effect vanishes after annealing. It is seen that as T_a rises, the peak shifts toward the glass transition and starts to overlap with it at the largest annealing temperatures. This phenomenon is consistent with the idea of the common relaxation spectrum for the β - and α -relaxations. Annealing at $T_a = 30$ °C initiates mostly the short time β -modes of the spectrum that relax rather independently of the other modes. As a result, the enthalpy recovery endo-peak appears below the main α -relaxation. Annealing at the high temperatures (e.g., 70 °C for PS and 80 °C for nPS90) initiates the longer time relaxation modes associated with the α -relaxation. Therefore, the recovery peak overlaps with the glass transition.

As mentioned earlier, the TNM and KAHR models have not been generally successful in describing deep quenches that give rise to the sub- T_g peaks. However, it would be unfair not to mention a work by Hodge and Berens,²¹ who applied the TNM model to fit simultaneously the main α -relaxation process and the sub- T_g peak. Note that the suggested procedure first evaluates the effective activation energy and preexponential factor from the main α -relaxation event and then varies the x and β parameters to fit the overall data including the sub- T_g peak. Obviously, their procedure inevitably eliminates the very opportunity of individually evaluating the activation energy of the sub- T_g process should it be different from that of the α -relaxation.

To estimate the effective activation energy from the sub- T_g peaks, we use the peak shift method suggested by Chen²⁸ and by Bershtein et al.^{9,10} The respective equation is as follows:

$$E = -R \frac{d \ln \beta}{dT_p^{-1}} \quad (1)$$

where R is the gas constant and T_p is the peak temperature of the recovery peak. The method has been used in a large number of publications by Bershtein et al. and by Chen et al. and appears to be an established routine. The validity of the approach was verified experimentally for a number of polymers studied by Bershtein and Yegorov,⁹ who demonstrated that the E values obtained by eq 1 from the sub- T_g peaks are in good agreement with the activation energies of the β -relaxation obtained from dynamic mechanical and dielectric experiments.^{9,10} It should, however, be noted that interpretation of the E values obtained by such methods should be done cautiously because the value of T_p depends generally on the thermal history of the glass, i.e., on the conditions of cooling, annealing, and heating. For this reason, the resulting E value may be affected significantly by the thermal history and, therefore, has a meaning of the temperature coefficient of relaxation that may but does not have to be identical with the activation energy, which is usually interpreted in terms of the free energy barrier. With regard to this we should note that the effect of the thermal history should be significantly smaller in the case of the β -relaxation than α -relaxation. Different thermal histories obviously give rise to different glass structures that are associated with respectively different distributions of free volume. Aging at temperatures far below T_g relaxes predominantly the short time local-chain modes associated with the β -relaxation. The β -relaxation is a thermally activated Arrhenius process, which is noncooperative and, therefore, should be relatively independent of free volume and, therefore, of the structure. In particular, Donth¹⁵ provides evidence that the β -relaxation is nearly independent of free volume variations. On the contrary, the α -relaxation because of its cooperative nature should be strongly structure dependent.

An obvious key to obtaining the temperature coefficients that give reasonable estimates for the activation energy of the β -relaxation is the use of the lowest feasible temperatures and annealing times. The effect of the thermal history will definitely increase with increasing the temperatures and times of annealing that engage slower modes of the cooperative α -relaxation. However, even in this case the resulting E values may still provide some sensible information. In this regard we should mention one of the early theories of the glass transition in polymers that was developed by Wunderlich et al.²⁹ from the hole theory of liquids. In this theory the activation energy is estimated by eq 1, where T_p is the temperature for the C_p peak for the glass transition. It was found²⁹ that the E value depends on the previous cooling rate (higher cooling rates led to higher values of E), which suggested the existence of a hole-size (i.e., free volume) distribution, characterized by different activation energies and relaxation time spectra.

Recognizing that interpretation of the E values obtained by eq 1 may be arduous, we believe that they can be used in a rather straightforward manner for the purpose of semiquantitative comparison of the two present systems obtained under similar thermal histories. The plots of $\ln \beta$ against T_p^{-1} are shown in Figures 3 and 4. The values of T_p have been determined from DSC curves (Figures 1 and 2) after subtracting a baseline that has been interpolated via a spline function. It is seen (Figures 3 and 4) that the plots are linear, which is a feature

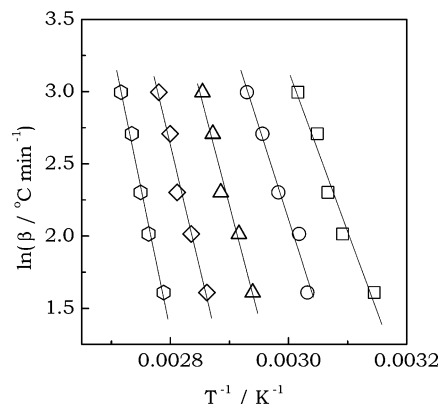


Figure 3. Evaluating activation energies (eq 1) for β -relaxation in PS100 (squares, $T_a = 30$ °C; circles, $T_a = 40$ °C; triangles, $T_a = 50$ °C; diamonds, $T_a = 60$ °C; hexagons, $T_a = 70$ °C).

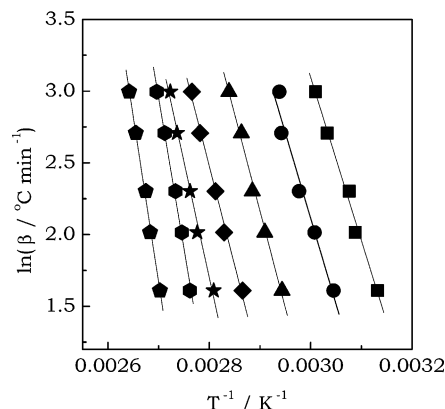


Figure 4. Evaluating activation energies (eq 1) for β -relaxation in nPS90 (squares, $T_a = 30$ °C; circles, $T_a = 40$ °C; triangles, $T_a = 50$ °C; diamonds, $T_a = 60$ °C; stars, $T_a = 65$ °C; hexagons, $T_a = 70$ °C; pentagons, $T_a = 80$ °C).

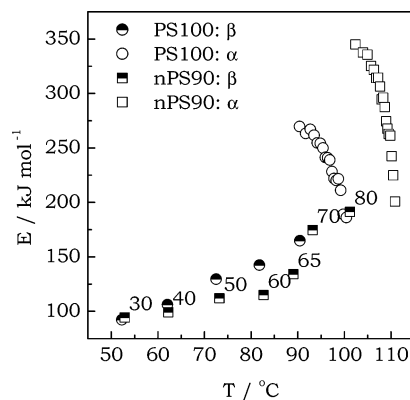


Figure 5. Variation of the activation energies for the α - and β -relaxation with average temperature of the process. Numbers by the points represent annealing temperatures.

typical of β -relaxations, which normally obey the Arrhenius law.^{15,30} The slopes of the plots tend to increase with the annealing temperature. Figure 5 displays a dependence of the effective activation energy of the sub- T_g peak on its average temperature. The latter has been estimated as an average of the T_p values obtained at different heating rates. At the lowest $T_a = 30$ °C both systems show the E value of about 90 kJ mol⁻¹, which agrees with 100 kJ mol⁻¹ obtained by Bershtein and Egorov,^{9,10} who used similar experiments and eq 1. The value falls in the middle of the range of the activation energies that were obtained from dielectric (120³¹ kJ mol⁻¹) and dynamic mechanical (70³² and 145³³ kJ mol⁻¹) measurements for the

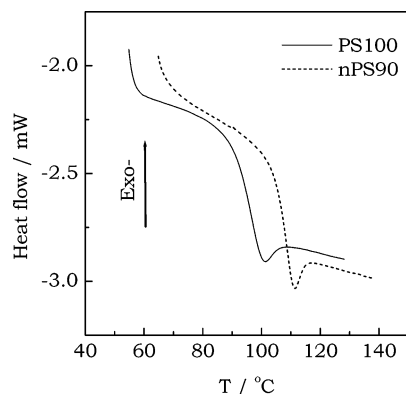


Figure 6. DSC curves for the glass transition (α -relaxation) in PS100 and nPS90 measured at $10\text{ }^{\circ}\text{C min}^{-1}$.

β -relaxation as well as from viscosity measurements ($80^{34}\text{ kJ mol}^{-1}$) performed in the sub- T_g region ($\sim 30\text{--}50\text{ }^{\circ}\text{C}$). Our value is also consistent within the respective uncertainty with the empirical relation between T_g and the activation energy of the β -relaxation ($E = 24RT_g$) that was established by Kudlik et al.³⁵ and theoretically supported by Ngai and Capaccioli.³⁶

The effective activation energy of the relaxation increases for both PS100 and nPS90 with increasing temperature. The increase is consistent with the idea of gradually engaging the longer time relaxation modes that become more and more associated with the cooperative molecular motion, which is characteristic of the α -relaxation. From the standpoint of the physical aging process, the observed increase in the effective activation energy means that at the temperatures above the β -relaxation the aging rate should become more temperature sensitive, i.e., should accelerate faster with the temperature. This fact has been observed experimentally by Venditti and Gillham.³⁷

In the nPS90 system, the increase in E occurs much slower than in PS100. As a matter of fact, there is no significant increase up to $T_a = 60\text{ }^{\circ}\text{C}$. That is, the β -relaxation in the PS-clay system is more decoupled from the α -relaxation than in the case of the virgin PS. This has an important implication for physical aging, as in the same temperature region the process in the PS-clay system should be less temperature sensitive than in virgin PS.

In conclusion, we should notice a remarkable similarity of the observed temperature dependence (Figure 5) to the temperature dependence of the effective activation energy for viscous flow as well as for stress relaxation that also shows a significant increase on approaching the glass transition region, after which it drops down to a smaller value. This effect has been originally predicted in the framework of the free volume concept by Fox and Flory³⁸ and somewhat later observed experimentally by McLoughlin and Tobolsky.³⁹

Glass Transition or α -Relaxation. DSC data for both materials demonstrate (Figure 6) typical glass transition steps, the midpoint of which has been used as an estimate of the T_g value. It is seen that in nPS90 the glass transition occurs at about $10\text{ }^{\circ}\text{C}$ greater temperature than in PS100. The values of T_g have been determined at nine heating rates (two times at each heating rate). The heating rate dependence of T_g can be used to evaluate the effective activation energy of the glass transition from eq 2,

$$E = -R \frac{d \ln \beta}{dT_g} \quad (2)$$

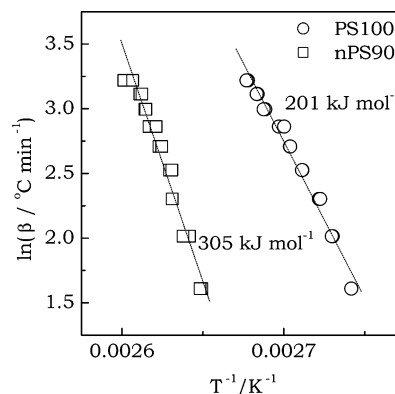


Figure 7. Evaluating activation energies (eq 2) for α -relaxation in PS100 and nPS90.

as proposed by Moynihan et al.^{40,41} A necessary constraint of eq 2 is that the samples must be heated at a rate whose absolute value is equal to the rate of preceding cooling.^{40,41} The resulting dependencies of $\ln \beta$ versus T_g^{-1} are shown in Figure 7. The plots are nonlinear, which is typically observed for the α -relaxations.^{15,30} The effective activation energy decreases with temperature, which is consistent with the general tendency predicted by the WLF equation:^{42,43}

$$E = 2.303R \frac{c_1 c_2 T^2}{(c_2 + T - T_g)^2} \quad (3)$$

where c_1 and c_2 are the constants. Forcing data to an Arrhenius plot yields averaged values of the effective activation energy for PS100 and nPS90 that respectively are 201 and 305 kJ mol^{-1} .

To determine a variation of E with the extent of conversion from the glassy to rubbery state, α , we have used an advanced isoconversional method.^{44,45} The method offers two major advantages over the frequently used methods of Flynn and Wall⁴⁶ and Ozawa.⁴⁷ First, it has been designed to treat the kinetics that occur under arbitrary variation in temperature, $T(t)$, which allows one to account for self-heating/cooling detectable by the thermal sensor of the instrument. For a series of n experiments carried out under different temperature programs, $T_i(t)$, the activation energy is determined at any particular value of α by finding E_α , which minimizes the function

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (4)$$

where

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (5)$$

The second advantage is associated with performing integration over small time segments (eq 5), which allows for eliminating a systematic error⁴⁵ occurring in the Flynn and Wall and Ozawa methods when E_α varies significantly with α . In eq 5, α is varied from $\Delta\alpha$ to $1 - \Delta\alpha$ with a step $\Delta\alpha = m^{-1}$, where m is the number of intervals chosen for analysis. The integral, J in eq 4, is evaluated numerically by using the trapezoid rule. The minimization procedure is repeated for each value of α to find the dependence E_α on α . Isoconversional methods determine the E_α values independently of the preexponential factors, which are not produced directly by these methods. It allows one to

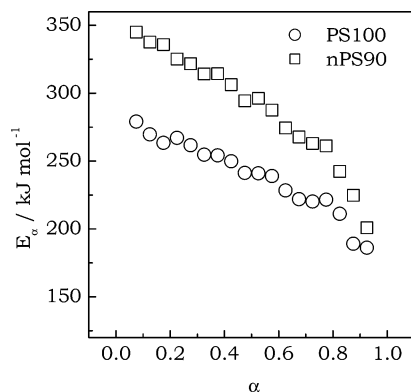


Figure 8. Variation of the activation energy for α-relaxation with the extent of relaxation.

eliminate the bias in the value of the activation energy caused by its strong correlation with the preexponential factor that is generally found when both parameters are fit simultaneously.⁴⁸

The conversion, α, can be evaluated from DSC data (Figure 6) as the normalized heat capacity⁴⁹ as follows:

$$C_p^N = \frac{(C_p - C_{pg})}{(C_{pe} - C_{pg})|_T} \equiv \alpha \quad (6)$$

where C_p is the observed heat capacity, and C_{pg} and C_{pe} are respectively the glassy and equilibrium (liquid) heat capacity. Because the values of C_{pg} and C_{pe} are temperature dependent, they must be extrapolated into the glass transition region. According to Hodge,⁴⁹ the C_p^N value provides a precise approximation to the temperature derivative of the fictive temperature. The application of the isoconversional method to the resulting α versus T data obtained at different heating rates yields the E_a dependencies shown in Figure 8. The activation energies decrease from 280 to 140 kJ mol⁻¹ for PS100 and from 350 to 160 for kJ mol⁻¹ for nPS90. Note that the values obtained for PS100 fall within the large interval, 160–900 kJ mol⁻¹, reported in the literature.^{32,33,49–52}

The E_a versus α plots can be converted into E_a versus T plots by replacing α with the temperature that is an average of the temperatures related to this α at different heating rates. The resulting plots are shown in Figure 5. This figure demonstrates a general tendency in the temperature variation of the effective activation energy of relaxation as the examined systems pass through the temperature regions of the β- and α-relaxation. It is seen that the value of E increases quickly when reaching the region of α-relaxation. The β-relaxation is frequently associated with the conformational motion (e.g., trans-gauche rotation and torsion)^{10,30} that occurs within a certain segment of the polymer chain. As the temperature rises, the amplitude of the local motions increases and they start involving translational motion of the segment and eventually of the whole chain at the glass transition. This process requires an increasing degree of cooperativity between the chain segments, which is associated with an increase in the energy barrier to the segmental motion as reflected in the effective value of E (Figure 5). For PS100 the maximum E value for the α-relaxation, ~270 kJ mol⁻¹, represents mostly cooperative translational motion, whereas the minimum E value for the β-relaxation, ~90 kJ mol⁻¹, represents mostly conformational motion. The ratio of these values is ~3, which is consistent with the general ratio, 4 ± 1 , found¹⁰ for the activation energies of the β- and α-relaxation in many polymers. During the glass transition the E value decreases with temperature. The decrease is caused by decreasing the density

of the studied polymers. When the packing becomes looser, the chain segments may relax in a more independent fashion, which requires a lower degree of cooperativity.

It should be stressed that the respective activation energies for the glass transition in nPS90 are markedly greater than in PS100 throughout the whole glass transition region (Figure 8). This suggests that the translational motion in the polymer–clay system requires a larger degree of cooperativity. The extra cooperativity in nPS90 is obviously introduced by the clay sheets that anchor several polymer chains, making their individual motions mutually dependent.

Note that the observed variation in E suggests that the α-relaxation is associated with a distribution of the activation energies that contradicts the assumption of thermorheological simplicity, which is the basic assumption of the TNM and KHR models. The general validity of this assumption has been repeatedly questioned,^{23,24} although it is still widely believed to be a reasonable approximation. The breakdown of thermorheological simplicity for the α-relaxation in PS has also been reported by O'Reilly and Hodge⁵³ and by Roland et al.⁵⁴ as significant systematic variations of the stretch exponent in the TNM model. On the other hand, the relaxation of PS is known⁴³ to reasonably obey time–temperature superposition, which is usually considered as evidence of thermorheological simplicity. The contradiction between these two types of experimental results can be explained in many cases by the fact that time–temperature superposition is not a very sensitive tool for detecting a distribution in the activation energies. The logarithmic transformation associated with the superposition largely smoothes away the systematic differences in individual relaxation curves, which become practically undetectable within the experimental uncertainty unless measurements cover a wide temperature region.⁵⁵ However, the relaxation measurements are most frequently carried out within a rather narrow region (e.g., about 30 °C for PS⁴³).

Volume of Cooperatively Rearranging Regions. On the basis of the results discussed in the previous section, the polymer–clay system should have a larger region of cooperative rearrangement. Donth has demonstrated that the volume of the cooperatively rearranging region at the glass transition can be estimated from calorimetric data by using the following equation:^{15,56}

$$V_g = \frac{k_B T_g^2 \Delta(C_v^{-1})}{\rho (\delta T)^2} \quad (7)$$

where k_B is the Boltzmann constant, T_g is an apparent glass transition temperature, ρ is the density (1.05 g cm⁻³ for PS⁵⁷), and C_v is the isochoric heat capacity. The value of $\Delta(C_v^{-1})$ is determined as

$$\Delta(C_v^{-1}) = C_{vg}^{-1} - C_{vl}^{-1} \quad (8)$$

where C_{vg} and C_{vl} are the respective values of the glassy and liquid heat capacity extrapolated to T_g . The difference between isochoric and isobaric heat capacities is usually neglected⁵⁶ so that C_v can be replaced with C_p , which is readily obtainable from calorimetric measurements. More recently, Hempel et al.⁵⁸ demonstrated that the difference can be accounted via the following correction:

$$\Delta(C_v^{-1}) = (0.74 \pm 0.22) \Delta(C_p^{-1}) \quad (9)$$

If the glass transition is measured on heating, the mean

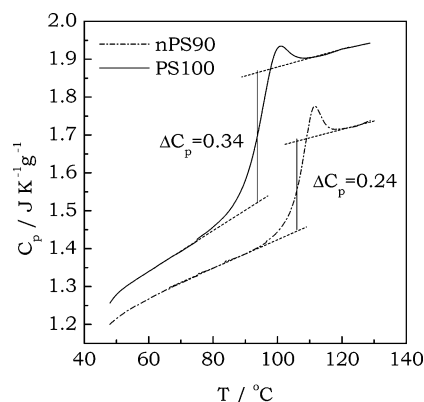


Figure 9. Temperature dependence of the heat capacity for PS100 and nPS90.

TABLE 1: Size of Cooperatively Rearranging Region and Experimental Parameters Used for Its Calculation

sample	T_g , K	C_{pg} , J K ⁻¹ g ⁻¹	C_{pl} , J K ⁻¹ g ⁻¹	δT , K	V_g , nm ³
PS100	366.9	1.53	1.87	2.6	20.9
nPS90	379.4	1.45	1.69	1.9	36.7

temperature fluctuation, δT , is estimated as

$$\delta T = \frac{\Delta T}{2.5} \quad (10)$$

where ΔT is the temperature interval within which C_p varies between 16 and 84% of the total ΔC_p step at T_g .^{56,58}

Figure 9 shows the results of our C_p measurements for PS100 and nPS90. The values of C_p for PS are in very good agreement with the earlier measurements.^{59,60} It is seen that the C_p values for the PS–clay system are noticeably smaller than for virgin PS. The decrease cannot be explained by the simple presence of clay because it is present in a very small amount (1%) and its heat capacity⁶¹ is comparable to that of PS. On the other hand, the value of the heat capacity is proportional to the number of internal degrees of freedom of molecular motion. Since anchoring of PS chains should unavoidably decrease the number of the degrees of freedom, one should expect the PS–clay system to have a lower value of the heat capacity. It is also noteworthy that the decrease is more significant for the heat capacity of the liquid state than of the solid state.

By applying eqs 7–10 to the heat capacity data (Figure 9), we have evaluated the volume of cooperatively rearranging regions for PS100 and nPS90 (Table 1). For the PS–clay system the value of V_g is 1.8 times larger than for virgin PS. This result obviously supports the conclusion of the previous section that the translational motion in the polymer–clay system requires a larger degree of cooperativity at the glass transition.

The value $\xi = (V_g)^{1/3}$ gives the characteristic length of the cooperatively rearranging region.^{15,56} According to our data for PS100 (Table 1), ξ is 2.8 nm, which agrees well with the value 3.0 nm recently reported by Hempel et al.⁵⁸

Conclusions

DSC can be used to determine the activation energies of the α - and β -relaxations and for evaluating the sizes of cooperatively rearranging regions at the glass transition in polymer–clay systems. The obtained data indicate that the presence of the clay phase does not affect significantly the β -relaxation, although it appears to be more decoupled from the α -relaxation in the PS–clay system than in virgin PS. A dramatic difference from virgin PS has been observed for the α -relaxation, which

demonstrates a significant increase in both effective activation energy and the size of the cooperatively rearranging region for the PS–clay system. Both values suggest that translational motion in the PS–clay system requires extra cooperativity. The effect is apparently introduced by the clay sheets that anchor several polymer chains, making their individual motions mutually dependent.

Acknowledgment. We thank Dr. Xiaowu Fan for providing a sample of nPS90. Partial support for this work from the Army Research Office under grant DAAD19-02-1-0190 is gratefully acknowledged.

References and Notes

- (1) Wunderlich, B. *Thermal Analysis*; Academic Press: Boston, 1990.
- (2) Bernazzani, P.; Simon, S. L.; Plazek, D. J.; Ngai, K. L. *Eur. Phys. J. E* **2002**, *8*, 201.
- (3) Efremov, M. Y.; Olson, E. A.; Zhnag, M.; Zhang, Z.; Allen, L. H. *Phys. Rev. Lett.* **2003**, *91*, 085703.
- (4) Park, J. Y.; McKenna, G. B. *Phys. Rev. B* **2000**, *61*, 6667.
- (5) Schonhals, A.; Goering, H.; Schick, C.; Frick, B.; Zorn, R. *Eur. Phys. J. E* **2003**, *12*, 173.
- (6) Wunderlich, B.; Bodily, D. M. *J. Appl. Phys.* **1964**, *35*, 103.
- (7) Illers, K.-H. *Makromol. Chem.* **1969**, *127*, 1.
- (8) Chen, H. S.; Wang, T. T. *J. Appl. Phys.* **1981**, *52*, 5898.
- (9) Bershtein, V. A.; Yegorov, V. M. *Polym. Sci. USSR* **1985**, *27*, 2743.
- (10) Bershtein, V. A.; Egorov, V. M. *Differential Scanning Calorimetry of Polymers*; Ellis Horwood: New York, 1994.
- (11) Arbe, A.; Richter, D.; Colmenero, J.; Farago, B. *Phys. Rev. E* **1996**, *54*, 3853.
- (12) Meier, R. J.; Struik, L. C. E. *Polymer* **1998**, *39*, 31.
- (13) Ngai, K. L. *J. Chem. Phys.* **1998**, *109*, 6982.
- (14) Johari, G. P.; Goldstein, M. *J. Phys. Chem.* **1970**, *74*, 2034.
- (15) Donth, E. *The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials*; Springer: Berlin, 2001.
- (16) Angell, C. A. In *Supercooled Liquids, Advances and Novel Applications*; ACS Symp. Ser. 676; American Chemical Society: Washington, 1997; p. 14.
- (17) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, R. J. *J. Polym. Sci.: Polym. Phys. Ed.* **1979**, *17*, 1097.
- (18) Tool, A. Q. *J. Am. Ceram. Soc.* **1946**, *29*, 240.
- (19) Narayanaswamy, O. S. *J. Am. Ceram. Soc.* **1971**, *54*, 491.
- (20) Moynihan, C. T.; Eastel, A. J.; DeBolt, M. A.; Tucker, J. J. *Am. Ceram. Soc.* **1976**, *59*, 12.
- (21) Hodge, I. M.; Berens, A. R. *Macromolecules* **1982**, *15*, 762.
- (22) Hutchinson, J. M. *Prog. Polym. Sci.* **1995**, *20*, 703.
- (23) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. *Appl. Phys. Rev.* **2000**, *88*, 3113.
- (24) McKenna, G. B.; Simon, S. L. In *Handbook of Thermal Analysis and Calorimetry*, v.3; Cheng, S. Z. D., Ed.; Elsevier Science: Amsterdam, 2002; p. 49.
- (25) Fan, X.; Xia, C.; Advincula, R. C. *Colloids Surfaces: A* **2003**, *219*, 75.
- (26) Fan, X.; Xia, C.; Advincula, R. C. *Langmuir* **2003**, *19*, 4381.
- (27) Vyazovkin, S.; Dranca, I.; Fan, X.; Advincula, R. *Macromol. Rapid Commun.* **2004**, *25*, 498.
- (28) Chen, H. S. *J. Non-Cryst. Solids* **1981**, *46*, 289.
- (29) Wunderlich, B.; Bodily, D. M.; Kaplan, M. H. *J. Appl. Phys.* **1964**, *35*, 95.
- (30) Matsuoka, S. *Relaxation Phenomena in Polymers*; Hanser Publishers: Munich, 1992.
- (31) Hedvig, P. *Dielectric Spectroscopy of Polymers*; J. Wiley: New York, 1977.
- (32) Gao, H.; Harmon, J. P. *Thermochim. Acta* **1996**, *284*, 85.
- (33) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover: New York, 1991.
- (34) Kobayashi, H.; Takahashi, H.; Hiki, Y. *J. Non-Cryst. Solids* **2001**, *290*, 32.
- (35) Kudlik, A.; Benkhof, S.; Blochowicz, T.; Tschirwitz, C.; Rössler, E. *J. Mol. Struct.* **1999**, *479*, 201.
- (36) Ngai, K. L.; Capaccioli, S. *Phys. Rev. E* **2004**, *69*, 031501.
- (37) Venditti, R. A.; Gillham, J. K. *J. Appl. Polym. Sci.* **1992**, *45*, 1501.
- (38) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
- (39) McLoughlin, J. R.; Tobolsky, A. V. *J. Coll. Sci.* **1952**, *7*, 555.
- (40) Moynihan, C. T.; Eastel, A. J.; Wilder, J. J. *Phys. Chem.* **1974**, *78*, 2673.

- (41) Moynihan, C. T.; Lee, S.-K.; Tatsumisago, M.; Minami, T. *Thermochim. Acta* **1996**, 280/281, 153.
- (42) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, 77, 3701.
- (43) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; J. Wiley: New York, 1980.
- (44) Vyazovkin, S. *J. Comput. Chem.* **1997**, 18, 393.
- (45) Vyazovkin, S. *J. Comput. Chem.* **2001**, 22, 178.
- (46) Flynn, H.; Wall, L. A. *J. Res. Nat. Bur. Stand.: A* **1966**, 70, 487.
- (47) Ozawa, T. *Bull. Chem. Soc. Jpn.* **1965**, 38, 1881.
- (48) Vyazovkin, S. *Int. Rev. Phys. Chem.* **2000**, 19, 45.
- (49) Hodge, I. M. *J. Non-Cryst. Solids* **1994**, 169, 211.
- (50) Boller, A.; Okazaki, I.; Wunderlich, B. *Thermochim. Acta* **1996**, 284, 1.
- (51) Schawe, J. E. K. *J. Polym. Sci. B* **1998**, 36, 2165.
- (52) Simon, S. L.; Sobieski, J. W.; Plazek, D. J. *Polymer* **2001**, 42, 2555.
- (53) O'Reilly, J. M.; Hodge, I. M. *J. Non-Cryst. Solids* **1991**, 131–133, 451.
- (54) Robertson, C. G.; Santangelo, P. G.; Roland, C. M. *J. Non-Cryst. Solids* **2000**, 275, 153.
- (55) Vyazovkin, S. Unpublished computations.
- (56) Donth, E. *J. Polym. Sci. B* **1996**, 34, 2881.
- (57) Van Krevelen, D. W. *Properties of Polymers*, 2nd ed.; Elsevier: Amsterdam, 1976.
- (58) Hempel, E.; Hempel, G.; Hensel, A.; Schick, C.; Donth, E. *J. Phys. Chem. B* **2000**, 104, 2460.
- (59) Karasz, F. E.; Bair, H. E.; O'Reilly, J. M. *J. Phys. Chem.* **1965**, 69, 2657.
- (60) ATHAS Database available at <http://web.utk.edu/~athas/databank/intro.html>.
- (61) Abu-Hamdeh, N. H. *Biosyst. Eng.* **2003**, 86, 97.