Structural Heterogeneity in Poly(methyl methacrylate) Glasses of Different Tacticity Studied by Thermally Stimulated Current Thermal Sampling Techniques

Bryan B. Sauer* and Young H. Kim

E. I. DuPont de Nemours and Company, Inc., Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0356

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ABSTRACT: The thermally stimulated current thermal sampling (TSC-TS) technique was used to study the cooperative glass transition like relaxations in different tacticity poly(methyl methacrylates) (PMMAs) including iso- and syndiotactic forms. We use the high sensitivity of the TSC-TS method to study these weak and sometimes overlapping relaxations at a frequency of about 10^{-3} Hz where one can resolve cooperative relaxations well below the main glass transition (T_g), even if the species are a minor fraction of the overall relaxing species. The magnitudes of the values of E_a are compared with a theoretical prediction as a function of temperature, showing that the low-temperature tail of the glass transition in conventional atactic (e.g., 45% syndiotriads) extends down to 15 °C, while in our highest syndiocontent PMMA (80% syndiotriads), the glass-transition-like relaxations only extend down to about 80 °C. Results taken from the literature also substantiate the results obtained here for atactic PMMA. The results are contrasted to those for bisphenol-A polycarbonate and other polymers and suggest that compositional heterogeneity, more specifically the presence of low T_g "pockets" of predominantly isotactic sequences, contributes to the broad glass transition extending almost 90 °C below the main glass transition in atactic PMMA.

Introduction

Because of its commercial and technological importance and apparent high purity, poly(methyl methacrylate) (PMMA) is the subject of a significant fraction of the literature on polymer relaxations and related studies. Certain aspects of its glassy state distinguish this polymer from others including a rather broad "main" glass transition[1−3] and other various properties related to tacticity. At low frequencies, the center of the glass transition (T_g) is about 105 °C in "conventional atactic" PMMA. For the pure tacticity forms of PMMA a large difference in T_g is found where isotactic PMMA has a T_g of about 45 °C, and syndiotactic PMMA has a T_g of about 130 °C at differential scanning calorimetry DSC frequencies.[4] The higher rotational barriers that cause the higher T_g in syndio-PMMA can be attributed to higher chain stiffness or stronger intermolecular interactions between polar vinyl groups because of the different chain packing in the glass. Not all polymers show these different T_g values. Polystyrene, for example, shows little difference in T_g between syndio- and isotactic forms, presumably because there are no polar groups. As can be inferred from the relatively high T_g of conventional atactic PMMA, it is predominantly syndiotactic, as can be shown by other direct techniques such as NMR described below. Observations of structural relaxations at room temperature, that could be explained by broad glass-transition-like relaxations extending almost 100 °C below the main T_g, have been made recently[5] and will be compared with thermally stimulated current thermal sampling (TSC-TS) studies of the broadened glass transition. The main purpose of this work is to use the sensitive TSC-TS technique to quantify the breadth of the glass transition and to verify the results by studying the pure tacticity forms.

The TSC thermal sampling (TSC-TS) or thermal windowing technique has been applied to polymers showing the capability of resolving complex dielectric transitions into narrow distributions of relaxations.[6−16] Reviews including very recent ones are available.[17−22] Several studies of the glass transition region in PMMA have been reported,[11,17,18,22−25] including reports where the TSC-TS technique was applied.[11,22−25] In general, explanations for the TSC-TS results and the relationship of the activated parameters to glass transition phenomena are somewhat controversial.[11,14,22,25] It is known that the TSC-TS method is uniquely sensitive in the case of weak or overlapping relaxations, where one can resolve "cooperative relaxations", e.g., those corresponding to high values of the apparent activation energy E_a, even if the species are a minor fraction of the overall relaxing species.[11,26] This high sensitivity to the high activation energy relaxing species is related mainly to the polarization and depolarization sequences used, and the method used for extracting E_a from the TSC-TS peaks, and will be discussed more quantitatively in a future report.[27] In this report we characterize the broad glass transition regions of PMMA of different tacticities in terms of the magnitude of the values of E_a. Comparison of the values of E_a with semiempirical predictions allows us to evaluate the breadth of the glass transition over a wide range of temperatures.

Experimental Section

Materials. Properties of the PMMA samples are given in Tables 1−3. Monodisperse PMM1 with $M_w = 480\,000$ was obtained from Pressure Chem. Co. and was studied by TSC previously.[11] Free radical PMMA (PMM2) with a molecular weight of about 100 000 was purchased from Aldrich. Group transfer polymerized PMM3 was an experimental sample.[28] PMM4 was purchased from PolyScience Co. and had a relatively high syndiotactic content. Syndiotactic PMM5 was prepared according to Hatada's procedure.[29] Isotactic PMMA (Iso-PMMA) was obtained from Scientific Polymer Products, Ontario, NY (catalog no. 689).

Samples for TSC consisted of films pressed by hand in the melt at low pressures. Sample history had no effect on the results in terms of cooling rate from the melt over the ranges that we examined. Iso-PMMA and PMM5 are semicrystalline

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Table 1. PMMA Sample Designations and Properties

		T_g(°C, DSC or TSC, ca.10^{-3} Hz)
PMM1	monodisperse $M_w = 480\,000$, $M_w/M_n = 1.1$	105
PMM2	atactic free radical PMMA, $M = 100\,000$	103
PMM3	group transfer polymerized PMMA at 50 °C	112
PMM4	high syndio PMMA from Poly. Science	118
PMM5	“syndiotactic” PMMA made by Hatada’s method	122
iso-PMMA	isotactic PMMA from Sci. Polymer Prod.	47

Table 2. Tacticity Determined from ^{13}C NMR

	triad[a]	tacticity obsd	p(r) or p(m)[b]	tacticity calcd
PMM2	rr	48.9	0.699	48.9
	mr	44.9		34.8
	mm	6.2	0.249	6.2
sum		100	0.948	89.9
PMM3	rr	47.7	0.691	47.7
	mr	42.5		28.3
	mm	4.2	0.205	4.2
sum		94.4	0.896	80.2
PMM4	rr	72.5	0.851	72.5
	mr	26.8		22.1
	mm	1.7	0.130	1.7
sum		101	0.981	96.3
PMM5	rr	80.3	0.897	80.3
	mr	18.4		8.4
	mm	<0.1	(0.104)	1.1
sum		98.7	1.0	89.9

[a] rr refers to the percent syndotriads, mr to atactic triads, and mm to isotriads. [b] p(r) is the probability of adding a monomer to form a racemic diad, indepedent to the configuration of the previously added monomer units, and p(m) is the probability of adding a meso unit.

Table 3. Long Range Tacticity Obtained from the Carbonyl Region

	PMM2	PMM3	PMM4	PMM5
m r r r	0.80	0.72	0.44	0.26
r r r r	1.00	1.00	1.00	1.00

and rather low crystallinity glasses were studied here, obtained by cooling from the melt at 100 °C/min. Film thickness also did not affect the TSC-TS results. For some thicker films (e.g., 0.5 mm), colloidal silver was painted on for the electrodes. For most of the samples, 0.1−0.2 mm thick films were sandwiched between spring-loaded steel disks used as electrodes. No difference was seen between the two geometries. The latter were generally not sputter coated with Au/Pd because artifacts were sometimes observed due to thermal stresses.

For tacticity determination, ^{13}C NMR spectra were obtained from about 0.2 wt/vol % polymer solutions in $CDCl_3$ at 75.575 MHz frequency, with 45° pulses and at least 3 s pulse delay. Pulses (64 000) were accumulated prior to processing. Methyl peaks and quartenary carbon peaks were used to estimate triad tacticities. The data shown in Table 2 are for the methyl 17−22 ppm. region. Peaks at the carbonyl region were not resolved enough to estimate pentad tacticity unequivocally. However, the peak intensity ratios between syndiotactic pentads, rrrr (178.0 ppm), and mrrr (178.1 ppm) sequences, which illustrate long range syndiotacticity propensity, can be seen to give strong distinctions between the different samples (Table 3). PMM5 is found to have significantly higher long range syndiotacticity than any of the other three samples (Table 3).

Methods. The TSC spectrometer (Model Solomat 41000, name of company has changed to TherMold Partners, Stamford, CT, and TSC Instrument is now TherMold TSC-RMA 9000 or 3000) was used as was described previously.[11] Both “global” TSC spectra and TSC-TS spectra were obtained.

For global TSC experiments the film is first heated to a temperature generally above T_g, e.g., the initial polarization temperature T_p, and then polarized by a static electric field ($E \sim 100-2000$ kV/m) for 2 min with continued polarization during cooling at 30 °C/min down to the “freezing temperature” T_o. Then the field is removed and the depolarization current (J) measured during heating at at 7 °C/min to a final temperature T_f ($\geq T_p$). J is due to a convolution of all dielectrically active relaxations over the temperature and frequency range probed.

Spectra in the TSC-TS mode were obtained using the standard procedure.[23,30] First, the polarizing field is applied for 2 min at T_p. With the field left on, the sample is cooled at 5 °C/min to $T_p - 5$ °C, and then the field is removed to depolarize for 2 min. at $T_p - 5$ °C. The sample is then quenched at 30 °C/min with the field off to about 40 °C below T_p. The TSC-TS depolarization current is then measured upon reheating at 7 °C/min to values about 40 °C above T_p. This same polarization sequence has been used our previous reports,[10,11,26,31,32] and the resulting activation energies, obtained as described below, are remarkably insensitive to small differences in the exact details of polarization sequence. In other words, the polarization parameters can be modified slightly but the TSC-TS technique will still accurately detect a narrow distribution of relaxations.

Background

Relaxation times $\tau(T)$ can be obtained using the standard “Bucci”[33] or “BFG” method. A slightly modified version of this method will be described below. For an ideal Debye relaxation with a single relaxation frequency, BFG relaxation times are defined by[17,18,33]

$$\tau(T) = P(T)/J(T) \tag{1}$$

where P is the remaining polarization. Using the definition of P[33]

$$\tau(T) = 1/\beta\{\int_T^{T_u} J(T')\,\mathrm{d}T'\}/J(T) \tag{2}$$

where β is the heating rate, T_u is an upper temperature where all current is released, and $J(T)$ is the depolarization current. The current peaks are integrated numerically to obtain the integral in eq 2. $\tau(T)$ is thus calculated at each temperature giving a “BFG” Arrhenius curve. The Solomat analysis uses a slightly modified form of the BFG method contrary to what is stated in our previous publications,[10,11,26] i.e., we have used the modified method described below even though it was stated in our papers that the BFG method was used. Furthermore, the limits of the integral in the “BFG” equations (e.g., eq 2) given in our previous reports are incorrect,[10,11,26,31,32] although the calculations were done correctly.

For distributed relaxations it is known that the BFG method gives low values of E_a,[17] although for properly cleaned peaks this can be a minor factor in obtaining accurate values of E_a because the distribution of relaxations is forced to be narrow by the narrow polarization windows used in the TSC-TS polarization sequence. For thermally cleaned or thermally sampled peaks with relatively sharp distributions of relaxations, one can apply an empirical correction. With the BFG method, curvature in the Arrhenius plot is generally seen well before the peak maximum, unless the peak is due to a single Debye relaxation.[17] The modified method will remove or reduce the curvature found in τ (T) vs $1/T$ BFG plots. The standard definition of P is

$$\beta P(T) = \int_T^{T_u} J(T')\,\mathrm{d}T' = \int_0^{T_u} J(T')\,\mathrm{d}T' - \int_0^{T} J(T')\,\mathrm{d}T' = \beta P_o - \int_0^{T} J(T')\,\mathrm{d}T' \quad (3)$$

The modified BFG method (eq 4) consists of dividing the total polarization (P_o) by a factor of 1.6 to correct for the fact that the total polarization is larger than it would be for a single Debye relaxation.[15,22]

$$\beta P(T) = \beta P_o/1.6 - \int_0^{T} J(T')\,\mathrm{d}T' \quad (4)$$

The modified value of $P(T)$ is then used in the BFG equation (eq 1). The value of 1.6 was derived previously,[15] and the method allows one to only obtain accurate values of $\tau(T)$ up to the peak maximum in the TSC-TS spectrum. Other TSC-TS peak fitting methods, which extract the distributions in E_a more directly without these approximations, have been shown to give equivalent results to those obtained by the modified BFG method.[10,11]

Using a depolarization heating rate of about 7 °C/min, the values of $\tau(T)$ fall in a range within 10^1 s $< \tau < 10^4$ s. They are typically analyzed using the Arrhenius equation

$$\tau(T) = \tau_o \exp(E_a/RT) \quad (5)$$

where τ_o is the pre-exponential factor and R is the ideal gas constant. One TSC-TS spectrum typically gives one value of E_a.

As is the case for relaxation data from any technique, the cooperativity can be determined by comparing with the "zero entropy prediction" of E_a which has no adjustable parameters and is determined from the rearranged Eyring's activated states equation[10,11,34,35]

$$E_a = \Delta H^{\ddagger} + RT = RT[1 + \ln(k/h) + \ln(T\tau)] + T\Delta S^{\ddagger}$$

and inserting the values of the constants

$$E_a = RT[22.92 + \ln(T/f)] + T\Delta S^{\ddagger} = RT[24.76 + \ln(T\tau)] + T\Delta S^{\ddagger} \quad (6)$$

where k is Boltzmann's constant(1.38×10^{-23} J K^{-1}), temperature is in degrees Kelvin, h is Plank's constant (6.6262×10^{-34} J s), and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activated states enthalpy and entropy, respectively.

$\Delta S^{\ddagger}$ is set equal to zero in eq 6, and f is the equivalent frequency of TSC of about 5×10^{-3} Hz.[17] Since the logarithm of f is taken in eq 6, typical variations in f lead to only small differences in E_a. For cooperative relaxations including glass transitions, the measured values of E_a depart from the $\Delta S^{\ddagger} = 0$ prediction and show a prominent maximum at T_g.[10,11] Equation 6 is also very useful to confirm the accuracy of the technique and analysis because measured values of E_a for low-temperature noncooperative relaxations should agree exactly with the $\Delta S^{\ddagger} = 0$ prediction.[10,11,34]

Results

Representative global TSC spectra are shown in Figure 1 for PMMA samples. Transitions detected by global TSC are characterized by a broad spectrum of relaxations, similar to low-frequency dielectric loss experiments. The β transition at about −30 °C is seen to be relatively consistent for three samples in the lower part of the plot, while the glass transition (or α transition) intensity varies slightly. The data for iso-PMMA are from Gourari et al.[24] and were also reproduced in our laboratory with our sample characterized by a slightly lower value of T_g (=47 °C). The low-temperature region shows the expected weak signal in the β transition region[36] and a strong glass transition at 52 °C (α). PMM2 is atactic with 49% syndiotriads (Table 2) and has the lowest T_g of 103 °C, and PMM4 is atactic but with slightly higher syndio content of 73% syndiotriads and T_g = 118 °C(Figure 1). PMM5 had the highest syndiotactic content of 80% syndio triads and a T_g of 122 °C. Above T_g for PMM2 and PMM4 a second peak can be seen. This is the low-temperature part of the ρ peak which has been only partially polarized because the maximum polarization temperature was only 140 °C for these experiments. The ρ peak has been extensively studied previously, with conflicting interpretations.[17,18,24] TSC is a direct current measurement, and accumulation of charges at buried interfaces (i.e., Maxwell-Wagner) or injection of charges (space charges) near the electrode surfaces lead to additional high-temperature transitions, mainly the ρ peak. The space charge mechanism was proved directly in PMMA by elegant experiments by van Turnhout.[17] The release of space charges is typically associated with mobility of polar charged impurities, which becomes high only above T_g.[17,18]

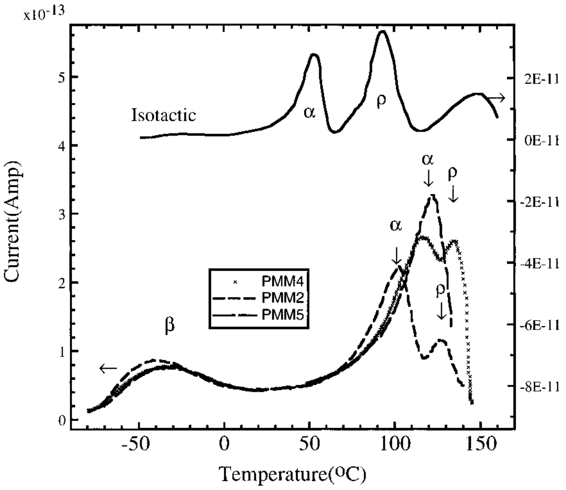

Figure 1. Global TSC spectra for Iso-PMMA taken from ref 24 and for three other PMMA samples obtained with $T_p = 140$ °C, $E = 400$ kV/m, were normalized to a sample area of 5 mm^2 with a thickness of 0.35 mm. The three samples were as follows: PMM2-atactic with 49% syndiotriads; PMM4-atactic but with higher syndio content of 73% syndiotriads; PMM5-"syndiotactic" with 80% syndiotriads. Properties are listed in Tables 1 and 2.

Using eq 4, one value of E_a is obtained from one TSC-TS spectrum, except in some cases, very close to T_g, two values are obtained from a single spectrum because of curved "BFG" Arrhenius plots for related reasons given earlier.[11,26] This does not change the trend in the results. Data for the three different PMMA samples in Figure 2 (top) indicate that the values of E_a depart from the $\Delta S^{\ddagger} = 0$ prediction starting as low as about 15 °C. A maximum in E_a is seen at the "low-frequency" T_g for each sample as is the case for almost every homopolymer or blend we have studied by the TSC-TS method. Figure 2 also shows the consistency of the TSC-TS technique where it is seen that Ibar's data taken in a different laboratory[25] on a different atactic PMMA sample (Figure 2, top) agree quite well with the data for our atactic PMMA (PMM1). Most importantly, the

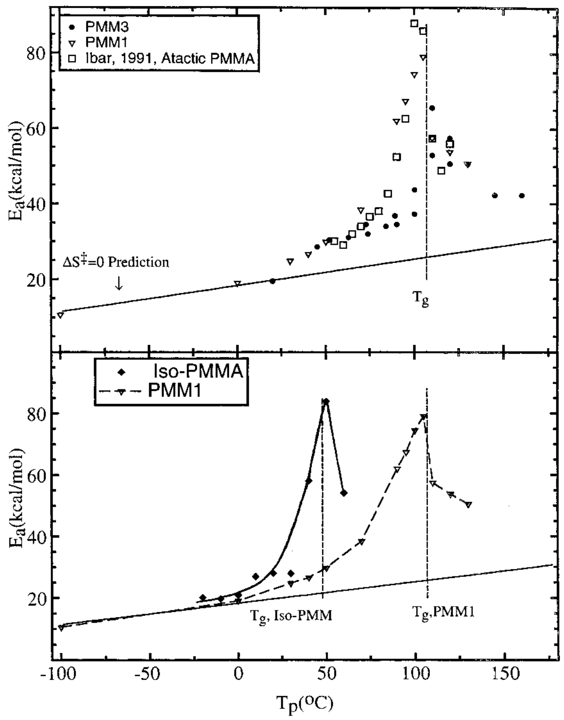

Figure 2. (top) Apparent activation energies versus polarization temperature obtained from the TSC-TS method showing a prominent maximum at T_g. Literature data[25] taken on a different sample show the same trend as that seen for conventional atactic (PMM1), illustrating the broad cooperative transition extending down to ca. 15 °C. For PMM3 (group transfer polymerized) the values of E_a are substantially lower between 75 and 100 °C (see text). Repeat data were taken for PMM3 over a period of 3 years and were found to be highly reproducible, as were the other data. (bottom) Values of E_a versus polarization temperature for atactic (PMM1) and iso-PMMA.

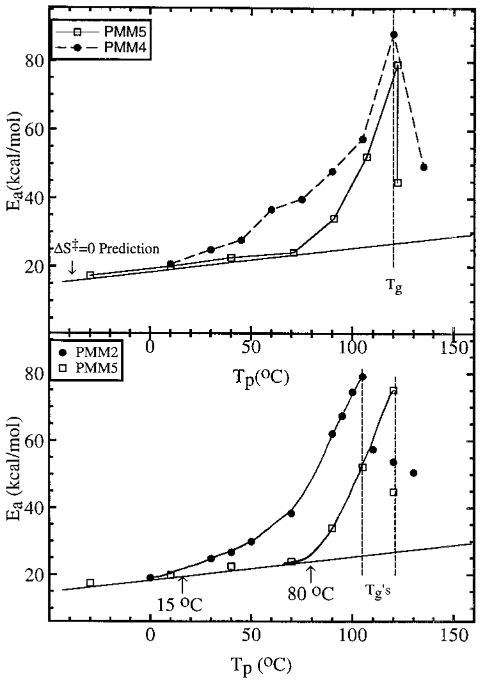

Figure 3. (top) Comparison of the two samples with the higher levels of syndiotacticity. The cooperative relaxations can be seen to extend down to substantially lower temperatures for PMM4 with the lower degree of syndiotacticity. (bottom) Values of E_a versus polarization temperature for conventional atactic (PMM2) versus syndiotactic (PMM5). The onset of departure from the $\Delta S^{\ddagger} = 0$ prediction extends to very low temperatures relative to T_g for PMM2, while it is somewhat sharper for PMM5.

literature data show the broad low-temperature tail detected as a departure from the $\Delta S^{\ddagger} = 0$ prediction extending well below 105 °C, although the literature values were not available below 55 °C. PMM3 (group transfer polymerized) has a slightly higher T_g (Table 1) which causes a slight shift in the maximum in E_a (Figure 2, top). The values of E_a are substantially lower compared to PMM1 between 75 and 100 °C, possibly indicating that the polymer chains are more homogeneous in terms of their structural regularity and/or composition. Data were taken for PMM3 over a period of 3 years and were found to be highly reproducible as is indicated by the repeat experiments at a few temperatures in Figure 2 (top). Figure 2 (bottom) compares the data for iso-PMMA with those for atactic PMM1, showing that the low-temperature side of the departure from the $\Delta S^{\ddagger} = 0$ prediction is broader for PMM1.

Data for the two samples with the higher levels of syndiotacticity are compared in Figure 3 (top), where PMM5 is our sample with the highest syndiotacticity. Departure from the $\Delta S^{\ddagger} = 0$ prediction extends down to substantially lower temperatures for PMM4 than for PMM5. This is the most dramatic evidence that a fraction of sequences high in isotactic content, with their inherently lower T_g, are relaxing cooperatively well below the main T_g of about 105 °C in conventional "atactic" PMMA. The conclusion is also consistent with the sharper transition seen for iso-PMMA in Figure 2 (bottom). PMMA is one of the few polymers with a large difference in T_g for the pure tactic forms, e.g., isotactic PMMA has a T_g of about 45 °C, and syndiotactic PMMA has a T_g of about 130 °C, so these phenomena will not be seen in all polymers.

Values of E_a are plotted for conventional atactic (PMM2) versus our high syndiotactic sample (PMM5) (Figure 3, bottom). The onset of departure from the $\Delta S^{\ddagger} = 0$ prediction extends to very low temperatures for PMM2, while it is somewhat sharper for PMM5. Because of the shift in T_g due to the higher syndio content of PMM5, the trend is not as dramatic as it is for the two samples in Figure 3 (top).

Discussion

Although the TSC-TS method has been applied to polymer relaxations for many years[23,30] and has been shown to be effective at experimentally separating broad relaxations into narrow distributions, only more recently have the values of E_a obtained with the technique become more consistent in the literature. From the early times it has been known that maxima, or at least steep increases in E_a,[23,30,37,38] are detected due to cooperative relaxations near T_g. Literature results[11] for bisphenol-A polycarbonate (Lexan film), a standard amorphous homopolymer, are shown in Figure 4 and are compared with the data for conventional atactic PEMA and PMMA. The onset for the departure of E_a from the $\Delta S^{\ddagger} = 0$ prediction is very abrupt on the low-temperature side of the glass transition for Lexan (DSC T_g = 147 °C). The data for PEMA and PMMA show a strong departure of E_a from the $\Delta S^{\ddagger} = 0$ prediction well below their main T_g values, showing that cooperative relaxations are occurring well below "T_g" (Figure 4). Similar to Lexan, the majority of amorphous homopolymers and moderate crystallinity semicrystalline polymers give rise to very sharp increases in E_a near T_g.[10−13,16,30] The sharp onset is even seen in completely

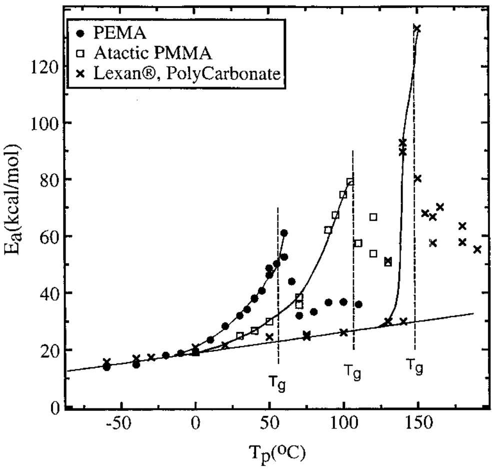

Figure 4. Typical results for a glass with a sharp increase in E_a at the glass transition (Lexan) as compared to conventional atactic PEMA and PMMA. The acrylates show a broad increase in cooperative relaxations starting well below their respective "T_g" values. The onset for the departure of E_a from the $\Delta S^{\ddagger} =$ 0 prediction is very abrupt for Lexan, as it is for many other homopolymers including semicrystalline ones.

miscible amorphous blends[32] but not in "atactic" PMMA and a few other "chemically heterogeneous" polymer glasses.[26,39] The values of E_a determined by a new analysis of ac dielectric data for poly(vinyl chloride)[40] also suggest that this material is chemically heterogeneous, probably again due to variable tacticity or other chemical heterogeneity.

Because of the broad low-temperature cooperative relaxations just below the main T_g in PMMA, intriguing compensation patterns of the BFG lines are seen in the Arrhenius plots.[11,22,24,25] In chemically heterogeneous systems such as atactic PMMA and other polymers,[26] this cannot be related to fundamental *bulk* material properties such as the thermal expansion coefficient, because the results are dominated by the cooperatively relaxing fraction which is a minor fraction below the main glass transition. Recent work suggests that compensation arises from covarience between the Arrhenius slopes and prefactors,[29] so the exact meaning of the compensation data is not completely understood.

In many dielectric studies at slightly higher frequencies, strong overlap is observed with the β and α (or T_g) transitions in PMMA and one might suspect that this is a cause of the broadened glass transition. This is probably not true for two reasons. First, the β and α transitions are clearly separated at the low TSC frequencies (Figure 1). More importantly, secondary localized relaxations such as the side chain rotation[36] (e.g., β transition) in PMMA are not cooperative and give values of E_a which agree with the $\Delta S^{\ddagger} = 0$ prediction by TSC-TS (Figure 3), and by conventional techniques.[35] The magnitude of E_a by TSC-TS is independent of peak current intensity. With a few exceptions,[41] for most polymers no departure from the $\Delta S^{\ddagger} = 0$ prediction is seen in the vicinity of secondary-low-temperature relaxations because of their non-cooperative nature.[11] This is the case for the low temperature region in Figure 3 for the strong β-relaxation at -35 °C in PMMA, and for the β-relaxation in Lexan, which is broad and occurs at about -130 °C at TSC frequencies[11] and is also "non-cooperative" in terms of the measured values of E_a in this region (Figure 4). The departure of the values of E_a from the $\Delta S^{\ddagger} = 0$ prediction in atactic PMMA (PMM1) in Figure 2 (bottom) in the region between zero and 60 °C correlates well with glass transition of iso-PMM (e.g., isotactic PMMA has a T_g of about 45 °C, Figure 1). We believe that this is due to the presence of a fraction of isotactic rich sequences with their inherently lower T_g in "atactic" PMM1, leading to cooperative relaxations of this small fraction well below the main T_g, which is about 105 °C for this sample. The correlation sphere for glass-transition-like motions has a radius of about 2 nm,[42] and it is certainly possible that pockets of isotactic rich sequences have an influence over these small dimensions. In physical blends of iso- and syndiotactic PMMAs, the homopolymers are borderline miscible as can be seen in very broad glass transitions in the blends.[4] It is not known whether the heterogeneity detected by TSC-TS is due to different distributions along individual chains or whether it is a result of different chains having different syndiotactic contents. The latter would be more similar to a polymer blend and the former to a blocky copolymer. This result verifies the conclusion that the typical "atactic" PMMA glass is actually quite heterogeneous, indicating that this material is probably not a good choice as a model polymer glass for relaxation studies.

We say that the fraction of cooperatively relaxing species is very small because DSC[2,3] and other techniques[1,36] do not detect this fraction below the main glass transition, although sensitivity for detecting these weak cooperative relaxations may be lower with other relaxation techniques because of the presence of other overlapping noncooperative relaxations and because of the large breadth[5] of the loss peaks associated with T_g in PMMA. We have obtained low-frequency (0.1 Hz) dynamic mechanical data (dynamic mechanical thermal analyzer, DMTA, Polymer Laboratories, MA) for PMM4 and PMM5 (not shown), where PMM5 is syndiotactic. No difference is seen in the breadth of the α (T_g) loss peaks or the variation of the dynamic modulus between 0 °C and $T > T_g$. Extensive calorimetry,[3] dilatometry,[1] and small angle X-ray fluctuation data[1] indicate that the breadth of the "main" glass transition in PMMA is rather large (ΔT_g, 23, 25, and 45 °C, respectively) as is well-known. Still, below ca. 80 °C no significant evidence is seen for a low-temperature tail in the glass transition.

Muzeau et al.[5] have detected unexpected structural changes by dynamic mechanical analysis after aging below T_g in an atactic PMMA sample with a DSC T_g of about 123 °C. At aging temperatures of 23 °C the β transition region was affected (β peak maximum was detected at 20 °C at their frequency of 0.1 Hz). At an aging temperature of 90 °C, the α peak was affected more than the β peak. They showed that at 23 °C aging could not be conventional physical aging because it could be erased by heating to temperatures above the annealing temperatures but well below the "main" T_g. If the species that were undergoing "structural relaxation" in their experiments at 23 °C were effectively above their T_g because of this low-temperature tail in the glass transition, then this could actually be considered physical aging and explain the phenomenon. This would be consistent with the low-temperature cooperative glass-transition-like relaxations that we have detected extending down to at least 15 °C by the TSC-TS method in atactic PMMA. Future work will involve extracting overall fractions of cooperatively moving species at temperatures somewhat below the main T_g in materials like the methacrylates, by a more detailed analysis of the TSC-TS spectra.

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