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Nanoscale Characteristic Length at the Glass Transition in Confined Syndiotactic Poly(methyl methacrylate)

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ABSTRACT: The size of the cooperatively rearranging region (CRR) at T_g has been measured for syndiotactic poly(methyl methacrylate) confined between the layers of an organophilic montmorillonite (OMMT) according to the method developed by Donth. The results show that the size of the CRR is constrained by the layers and that it starts to decrease for interlamella spacings up to 6 times larger than the size of the CRR at T_g. This shrinkage of the CRR with the confinement distance is discussed in term of cooperativity in confined systems according to the nature of the interfacial interactions. Contrasting with T_g depression reported in previous studies for s-PMMA thin films, for which stronger interactions were at stake, a positive shift of T_g is recorded for the lowest distances. This behavior is ascribed to conformational rearrangements effects since weak interactions between the s-PMMA and the organophilic modified clay are expected.

Introduction

When confined in a geometry whose typical size is smaller than a few tens nanometers, polymer chain dynamics shows strong deviations from the bulk.[1] For weak interactions between the substrate and the polymer chains, it is usually reported that the glass transition temperature exhibits a depression whereas for strong interactions the opposite trend is generally observed. Although many attempts have been undertaken to explain these observations, no universal model has found acceptance so far. The problem is not as straightforward as it might be expected from these first statements since the confinement effect is often superimposed by effects due to surface interactions but also to the remaining influence of the preparation path.[2] Thus, even though in some model cases a direct relation is found between the nature of the interactions and the modifications in the $T_g(h)$ for thin films[3,4] or the dynamics in glass formers in zeolites pores,[5,6] most of the systems are more complicated.

One intriguing question in this phenomenon is the existence of a critical thickness h^*, below which a shift in T_g is recorded. Several endeavors have been undertaken to relate this critical thickness to a characteristic length scale such as (i) the end-to-end distance, R_{EE}, of the polymer coil in the bulk,[7] when the macromolecular mass $M_w > 514$ kg/mol and for M_w lower than 340 kg/mol; (ii) the skeleton rigidity related to C_∞;[8] and (iii) a spatial length scale[5,9] identified with the average size of cooperatively rearranging regions (CRR), first introduced by Adam and Gibbs.[10] Forrest and Mattsson,[11] considering the existence of an enhanced mobility at the free surface, assume that the higher rate of conformational transitions extends within the sample with a characteristic length ξ. By fitting the data of $T_g(h)$ with the expression $T_g = T_{g,bulk} + (2/h)\xi(T_g)(T_{g,surf} - T_{g,bulk})$ where $T_{g,bulk}$, $T_{g,surf}$, h are respectively the glass temperature of the polymer in the bulk, the glass temperature of the polymer at the free surface, and the layer thickness, they find a value of ξ at the glass transition temperature, $\xi_{(T_g)}$, consistent with the size of CRR at this temperature.[12] A CRR is defined by Adams and Gibbs as a subensemble of particles which upon a sufficient fluctuation can rearrange into another configuration independently of its environment. On cooling the sample, more cooperativity is needed between neighboring particles for the α relaxation process, and then the size of CRR increases and finally diverges near the Vogel temperature. For polymers, the so-called particles must be understood as monomer units.

Physically, the confinement of a glass former in a geometry (with a characteristic length scale L) should prevent the diameter of the CRR at a given temperature T_L to overcome the finite size L. As a result for $T < T_L$ there is an increase of the chain dynamics and a decrease of the glass temperature T_g compared to the bulk. This phenomenon is known as the hindered glass transition effect.[13] Thus, one should expect no influence of a confined geometry as long as the smallest length scale of the system is larger than the size of the CRR. However, experiments confining glass forming liquids in pores whose dimensions are in the range of 2−10 nm show that finite size effects is felt for pore size, up to 4 times larger than the CRR size.[14,15] We find in those experimental facts similarity with the existence of the critical thickness h^* evoked formerly.

In this paper, we present our experimental results concerning the determination of the size of CRR for confined s-PMMA. We use the method developed by Donth et al. from specific heat capacity experiments.[16] In the present study, to probe the glass temperature of thin films with conventional differential scanning calorimetry (DSC), we confine the polymer in clays. This way of confining the polymer presents equally the advantage to continuously vary the size of confinement according to the degree of intercalation and the preparation conditions. In a first step, we present the raw data concerning the evolution of N_α, the number of particles involved in a CRR as well as the size of these regions. Then in a second step, we report the T_g values

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as the size of confinement decreases and discuss the conformation of s-PMMA in confined geometry.

Experimental Section

Nanocomposites are prepared by adding to PMMA−chloroform solutions given amounts of Cloisite 15 A (a modified organophilic montmorillonite (OMMT) with ditallowdimethylammonium chains commercialized by Southern Clay Products Inc). The concentrations of PMMA solutions were always below the overlapping concentration C^*. 10.0 mL of the s-PMMA−chloroform solutions was equilibrated for 24 h at 20 °C. After the addition of Cloisite15A, the suspension was stirred for 3 h at 20 °C. This equilibrium time is sufficient for the s-PMMA chains to enter the nanoclays galleries during the swelling of the OMMT by chloroform. No further intercalation is determined by X-ray scattering for longer times. After chloroform was evaporated at room temperature, samples were dried under vacuum at 185 °C for 1 h. The thickness of PMMA layers is assessed assuming the clay nanolayers are fully dispersed and that the polymer forms a dense film on of the whole surface of the Cloisite whose specific area is 760 m^2/g (determined by the BET method). The characteristics of the s-PMMA used in this study are $M_n = 30.0$ kg/mol, $M_w = 37.5$ kg/mol, and the % of syndiotacticity is 78.2. The radius of gyration computed from the formula 1 is 41 Å.

$$\langle R_g \rangle = \frac{a\sqrt{C_\infty N}}{\sqrt{6}} \qquad (1)$$

with $C_\infty = 7.2$,[17] N is the average of bond in a PMMA chain, and a is the carbon−carbon distance taken as 1.54 Å.

The T_g is 110 °C, which is in between the T_g of an atactic PMMA (100 °C for 60% syndiotactic triads) and a highly syndiotactic one (130 °C for more than 85% syndiotactic triads).

X-ray diffraction powder patterns were recorded using a Philips PW3710 diffractometer operating with Cu Kα radiation (1.5418 Å). X'PERT software, Data Collector, and Graphics and Identify were used respectively for pattern recording, analysis, and phase matching.

The size of the CRR can be computed from DSC experiments performed on a Mettler Toledo DSC from which specific heat capacities were drawn using sapphire as a reference. The sample weights are about 10 mg. The cooling−heating cycles were realized between $T_g - 90$ K and $T_g + 60$ K with rates of $|dT/dt| = \pm 10$ K/min. All the samples were annealed prior to the measurements in order to yield a reference state. Before any exploitation the raw data were normalized with respect to the polymer content. The characteristic length of cooperativity at T_g, $\xi_{(T_g)}$, and the number of particles, N_α, in the cooperatively rearranging volume are respectively computed according to Donth et al.[16] from the following expressions:

$$\xi = \sqrt[3]{k_b T^2 \frac{\Delta(1/C_v)}{\rho \delta T^2}} \qquad (2)$$

$$N_\alpha = \frac{\rho N_A \xi^3}{M_0} \qquad (3)$$

with N_α the number of particles in a CRR, N_A the Avogadro number, δT the mean temperature fluctuation, T the temperature, k_b the Boltzmann constant, ρ the polymer density (1.19 g/cm^3 for PMMA), C_v the volume specific heat capacity, and M_0 the molar mass of the particle. The particles are considered here as the methyl methacrylate monomer units.

The step of reciprocal specific heat capacity at constant volume at the glass transition is described as

$$\Delta(1/C_v) = (1/C_v)_{\text{glassy zone}} - (1/C_v)_{\text{liquid zone}} \qquad (4)$$

The approximation for the calculation of ξ from eq 3 neglects the difference between the heat capacities at constant pressure and the heat capacities at constant volume, so C_v can be replaced by C_p. By this way, we can determine, from DSC curves at T_g (Figure 1b), the values of $C_p{}^{\text{glass}}$, $C_p{}^{\text{liquid}}$, and ΔC_p. The mean temperature fluctuation of one average CRR for s-PMMA, δT, can be estimated by "a rule of thumb":[18] $\delta T = \Delta T/2.5$, where ΔT is the temperature interval where $C_p(T)$ varies between 16% and 84% of the total ΔC_p step at the glass transition (Figure 1a).

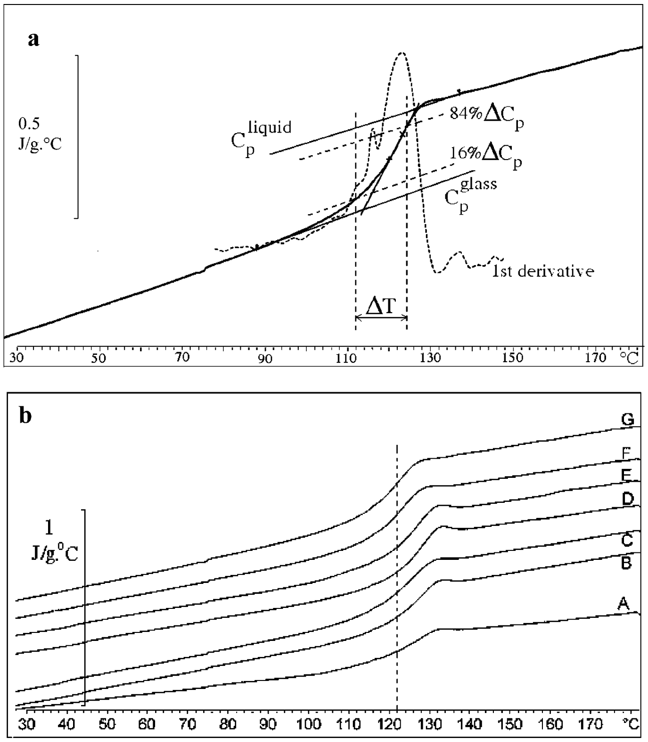

Figure 1. Specific heat capacity at constant pressure vs temperature. (a) Method used to determine ΔT from which the thermal fluctuation, δT, is calculated. (b) C_p curves for different clay content wt %. A (35%); B (19%); C (10.2%); D (5.2%); E (2.7%); F (1.4%); G (0.8%).

Results and Discussion

Figure 2 shows that Cloisite 15A exhibits a peak at 7.2° on the wide-angle X-ray scattering (WAXS) spectra which correspond to expected clay interlamella distance of 12 Å. When 35.3% of Cloisite 15A is dispersed in PMMA, two other peaks appear at 4.8° and 3.5°, which correspond to a distance of 18 and 25 Å, respectively. When the filler content decrease the peak at 7.2° vanishes as well as the one at 4.8° and at 0.8% of Cloisite, only the 3.5° peak remains. s-PMMA chains are therefore assumed to be more strongly confined at high nanofiller content, namely, for low equivalent estimated thickness The smallest thickness values found around 2 nm are consistent with the intercalation of the polymer in the clays galleries as measured by WAXS, indicating that intercalating s-PMMA in clay is an effective method of confinement.

From the raw DSC data shown in Table 1, it clearly turns out that the main modifications at T_g arise on the temperature fluctuation, δT more than on the change of step of specific heat capacity at T_g, ΔC_p, which is rather constant as a function of the film thickness. This is consistent with the observations made elsewhere for PS/MMT systems.[19] On the other hand, the enlargement of the temperature range of the glass transition is generally ascribed to an increase in the distribution of the relaxation times of various species in the polymer system. The number of particles involved in a CRR, N_α,

Table 1. Values Calculated from the DSC Curves for Different Amounts of Cloisite in the s-PMMA[a]

e (nm)	wt % Cloisite	T_g (K)	ΔC_p (J/(g K))	δT (K)	$\Delta(1/C_p)$ (g K/J)	$N_\alpha(T_g)$	V (nm^3) = ξ^3	ξ (nm)
2	35.8	401.4	0.42	7.0	0.0722	31	2.8	1.4
5	18	401.6	0.44	5.6	0.091	46	5.4	1.7
10	9.8	401.2	0.42	5.4	0.127	65	8.1	2
20	5.2	400.7	0.41	5.1	0.126	68	9	2.1
40	2.7	400	0.45	5.2	0.147	74	10	2.1
80	1.4	396.3	0.41	4.8	0.128	73	10.1	2.2
140	0.8	395.8	0.45	4.9	0.166	90	12.6	2.3
bulk	0	383.4	0.35	3.6	0.105	100	13.9	2.4

[a] Raw data have been normalized with respect to the polymer content.

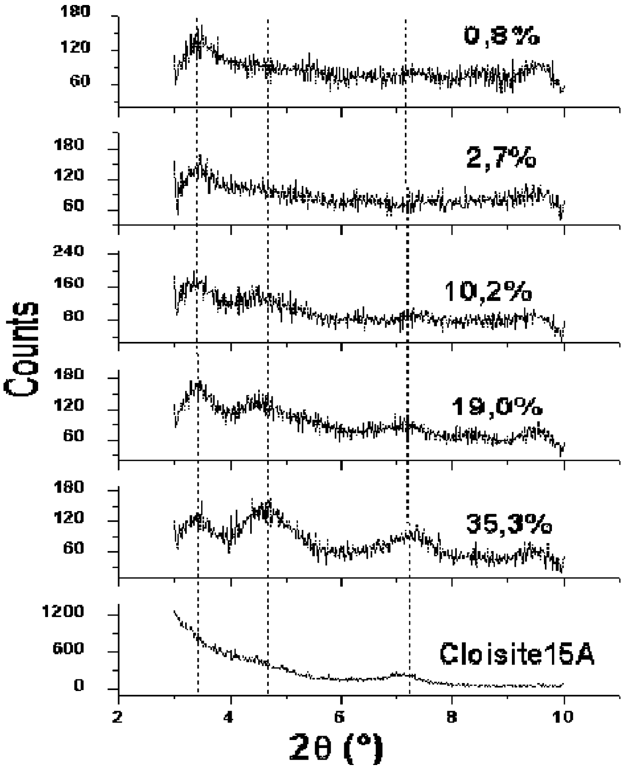

Figure 2. WAXS patterns of pure Cloisite 15A and s-PMMA/Cloisite 15A mixtures. The percentage indicated represents the amount of filler in the dry s-PMMA. The vertical dashed lines point the position of the peaks which are discussed in the text.

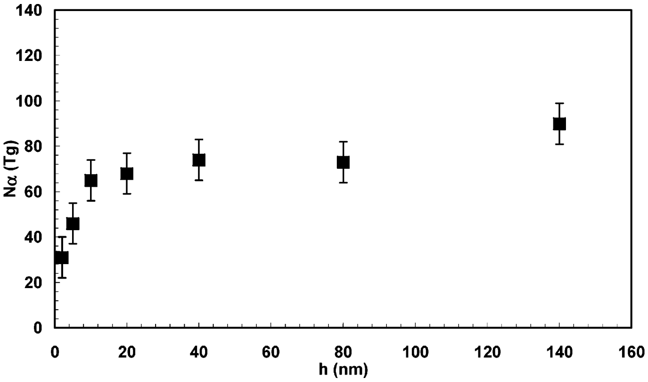

Figure 3. Evolution of N_α, the number of monomers in a cooperatively rearranging region, as a function of the length of confinement.

vs the assessed thickness is displayed in Figure 3. The bulk N_α value of 100 is consistent with values calculated by Donth[20] for acrylate and methacrylate systems. We clearly notice here a rapid decrease of the number of particles with the decrease of the estimated layer thickness. This deviation of N_α from bulk occurs for a thickness value, h', lying between 10 and 20 nm. The number of particles involved in a CRR decreasing with the confinement size can be explained on the basis of cooperativity. The key idea of cooperative models is the existence of a length scale of cooperativity that increases when the temperature is lowered. As the confining geometry is scaled down, the size of CRR is restricted and the number of particles involved in cooperative rearrangement decreases. This statement can be backed up by plotting in Figure 4 the dependence of $\xi_{(T_g)}$ vs h and the line $\xi(h) = h$. We clearly notice the constraint imposed by the clay interlamella spacing as for instance for very low gallery size, namely 1.5 nm, the size of the CRR is very close. This cooperativity at T_g which decreases in confined systems can be visualized as a lower necessary collection of polymer segments which must move together in a given time and space scale. In the absence of any other effects, this should therefore results in an enhanced molecular dynamic as well as T_g depression.[13,21] T_g variations vs the assessed thickness for PMMA nanocomposites are shown in Figure 5. We observe a positive shift, which contrasts with a depression of 25 K for syndiotactic PMMA thin films. To explain these discrepancies, several arguments have to be considered namely surface interaction and conformational effect. Moreover, preparation conditions might have an effect upon the amplitude of T_g shift as already noticed for thin films.[2,22]

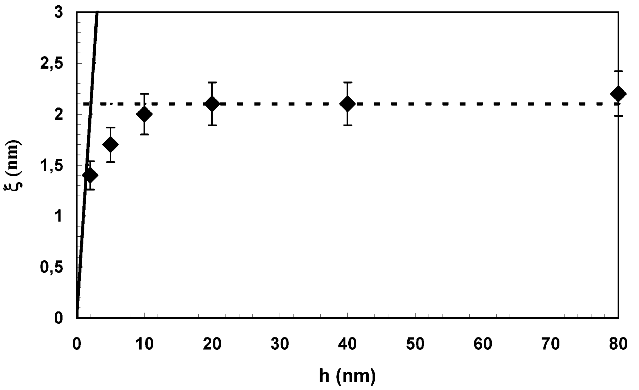

Figure 4. Evolution of the characteristic length $\xi_{(T_g)}$ vs the length of confinement.

The slight increase of T_g for s-PMMA nanocomposites observed here seems to contradict the observations made in thin films. To account for this apparent contradiction, one has to recall that the dynamics of a glass former is also influenced by surface interactions known to slow down the relaxation time.[5,6,23] T_g variation is thus the result of interplay between confinement and surface interactions, which are enhanced when the surface/volume ratio increases. This is exemplified by the results reported by Fryer et al.[4] By comparing the $T_g(h)$ shifts for the same atactic PMMA cast either on a

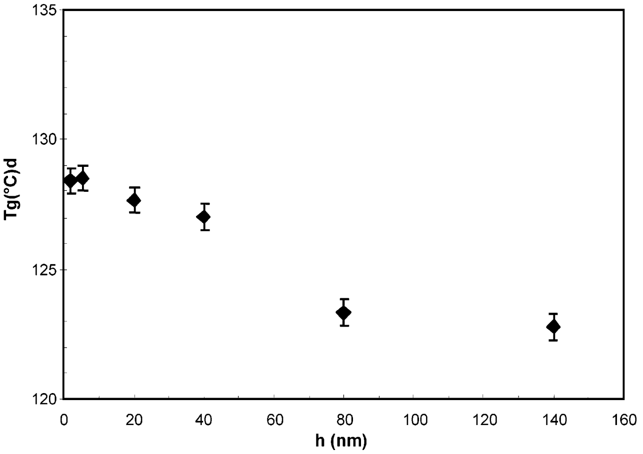

Figure 5. Evolution of the glass temperature T_g vs the length of confinement.

hydrophobic substrate (silanized silicon wafer with hexadimethyldisilazane) or on a SiO_x substrate, the authors measure in the former case a decrease of about 20 °C, whereas an increase of 8 °C was recorded in the latter. Similar results are obtained within the community working on glass forming liquids confined in porous media with a narrow nanopores distribution. Results obtained from NMR,[24,25] neutron scattering,[26,27] and dielectric relaxation measurements[6,28,29] give evidence of the superposition of populations with very different relaxation time. To account for the slower dynamics by 2 orders of magnitude for salol confined in nanoporous glass, Arndt et al.[26] have proposed a picture with a retarded layer of bound molecules near the surface vicinity and bulklike molecules in the center of the cavity. Schönhals et al.[6] on oligomers of poly(propylene glycol) and poly(methylphenylsiloxane) draw the same conclusion. As a consequence, results cannot be interpreted straightforwardly in terms of cooperativity. One way used to decouple these superposed effects is to lubricate the inner surface of the pores or of the confining surface. From a practical point of view this step is realized by converting the surface silanol groups into less hydrophilic trimethylsilyl groups. In those conditions, an acceleration of the dynamics is observed through the shift of the relaxation time distribution toward shorter relaxation time by 2 orders of magnitude. For small pores size, namely 2 nm, contrasting results are reported according to the system investigated. According to Schönhals et al.,[6] for poly(propylene glycol) ($M_w \sim 1000$ g/mol) confined to pore size larger than 3 nm confinement effects predominates, whereas for pores diameter inferior to 2 nm the dynamics is controlled by adsorption. For dihydroxylated propylene glycol the molecular dynamics is dominated by interaction of the hydroxyl groups with the surface for all pore size ranging between 2.5 and 20 nm. For silanized pores, the low relaxation process is not observed anymore. For salol confined to nanopores (2.5, 5.0, and 7.5 nm) with trimethylsilyl groups, Arndt et al.[5] show using broadband dielectric spectroscopy that the relaxation time distribution is shifted toward smaller relaxation time by 2 orders of magnitude whatever the chemical nature of the surface is. This effect is more pronouced for smaller pores. They ascribe the van der Waals glass former behavior of salol to preferential intramolecular interaction. This body of results clearly stresses the predominance of surface interactions for uncoated surface and small confining geometry. In our system, the surface of the organophilic montmorillonite are covered with quaternary ammonium dihydrogenated tallow chains of different length (65% C18, 30% C16, 5% C 14). Tallow chains screen silanol groups and one can think that the formation of H bonds between methacrylate and silanol groups are hindered. Thus, the strength of interfacial interactions between intercalated PMMA and tallow chains should be comparable to the interactions occurring at the inner surfaces of lubricated nanopores. Furthermore, in our case, no evolution of ΔC_p is observed even for low interlayer spacing. A decrease, for instance, of ΔC_p with the filler content would have meant a decrease of the number of species involved in the modification of the dynamic at the glass transition. This would have been consistent with the assumption of a "frozen layer" of polymer in contact with the surface. Thus, a direct interaction between the modified clay surface and the polar carbonyl groups of PMMA seems to be unlikely. However, surface effects can induce strong conformation modifications in the s-PMMA. This was already suggested by several authors[30−32] for s-PMMA on water, glass, or aluminum. The main conclusions drawn from these studies were that s-PMMA can behave as an amphiphilic polymer by allowing a selective surface exposure of nonpolar and polar functional groups as probed by wettability measurements.[31] Consistent results were obtained by the calculation of the conformation energy of s-PMMA/aluminum by IRRAS spectroscopy.[32] A large increase of the conformation energy was deduced for the thinnest films, which is the sign of strong conformational modifications. Finally, pressure−area isotherm performed on s-PMMA monolayers[30] at the water surface lead to the conclusion that this polymer yield condensed monolayer attributed to strong lateral cohesive interactions between the segments.

In the PMMA/OMMT systems confinement of the s-PMMA chains in nonpolar galleries should yield strong conformation modifications. Distortion of the polymer coil from a spherical shape is expected, but also very local scale conformation reorganization is assumed. A selective surface exposure of nonpolar (CH_2, αCH_3) groups can yield backbone and polar groups (COO) rearrangement which leads to an increase of intermolecular carbonyl group interaction inside the galleries. This spatial arrangement of the ester groups favoring strong dipolar interactions in s-PMMA were suggested by Vacatello[33] and Sundararajan[34] to be responsible for the high T_g of this stereoisomer as compared to the isotactic one. The slight increase of the $T_g(h)$ that is observed for our s-PMMA/OMMT system can be ascribed to the same effect induced by a combination of confinement and unfavorable surface effect. The direct relation between the local conformation and the size of the CRR according to the Adam and Gibbs approach has been discussed by Gomes Ribelles et al.[35] They found that the more available conformational state, the larger the size of the CRR is. The restriction of the conformation in the confined state will, therefore, decrease the CRR as observed in our study. Even though no formal experimental evidence of this conformational modification in confined system can be provided here, this complex effect cannot be ruled out.

Another point to be mentioned is the decrease of $\xi_{(T_g)}$ for a critical value h' up to 6 times larger than $\xi_{(T_g)}$ and the deviation of $T_g(h)$ from the bulk T_g at 60 nm, which is 6 times h'. This discrepancy between these two values is poorly understood and still require many theoretical investigations. The fact that polymers are equally sensitive to confinement length larger than the size of a CRR sets the question of the mechanism involved in this long-range influence and its dependence upon other characteristic of the macromolecular chain such as the entanglements for instance. Robertson et al.[36] very recently showed that the critical length between cross-links was very similar to ξ in elastomers. The possible correlation between the molecular weight between entanglements and ξ in thermoplastics will be the topic of our next paper.

Conclusion

The main goal of this work was to gain insight into T_g deviations observed in thin film of s-PMMA by confining the polymer between layered silicates and measuring the size of CRR at T_g when the interlayer spacing varies. We show that intercalation of s-PMMA in clay galleries is an effective method of confinement. The size of the CRR decreases with the length scale of confinement. However, contrasting with the results obtained with thin films of s-PMMA, we record an increase of T_g when the confining distance decreases. This behavior is ascribed to a restriction of the possible conformation in the confined state due to surface effects. We equally show that the distance involved in the variation of T_g and the size the CRR are not comparable. The mechanism involved in this long-distance effect remains an open question.

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