Glass transition properties of PMMA thin shells deposited on rodlike calcium carbonate particles

Takashi Sasaki,1 Rumi Kuroda,1 Mitsuhiro Teramoto,1 Shigeru Yonezawa,1 Hiromasa Tsuji,1 Kensuke Sakurai1 and Satoshi Irie2

ABSTRACT: Rodlike capsules consisting of a calcium carbonate core and a thin shell of poly(methyl methacrylate) (PMMA) were synthesized. The shell thickness $d$ ranged from 8 to 93 nm, and the degree of crosslink $X_c$ for the polymer shell ranged from 0 to 7.0wt%, where $X_c$ is defined as the mass content of the crosslink monomer (ethylene glycol dimethacrylate). The glass transition temperature $T_g$ and the length scale for dynamic heterogeneity at the glass transition $\xi(T_g)$ for the polymer thin shells were evaluated by temperature-modulated differential scanning calorimetry. It was found that $T_g$ is not altered from the bulk value for $d \geq$ ca. 20 nm for both filled and hollow shells. The thinnest non-crosslinked shell ($d = 8$ nm) exhibited a lowered $T_g$ from the bulk value. As for $\xi(T_g)$, no distinct dependence on $d$ was observed for non-crosslinked filled shells. Correlation between $\xi(T_g)$ and $T_g$ was also revealed, which is interpreted in terms of the concept of cooperatively rearranging region.

Keywords: capsules; PMMA; glass transition; crosslink

Running heads: Glass transition properties of PMMA thin shells

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INTRODUCTION

Thermal and mechanical properties of nano-sized polymeric materials have been attracted much attention in a wide range of technological areas concerning nano-devices, encapsulation, nanocomposites, coatings, and biomedical applications. From a practical point of view as well as of fundamental research on soft matter, it is becoming of great importance to understand the origin of the anomalous dynamics of nano-sized and nano-confined polymers that differs considerably from the bulk materials.\(^1\) Investigations to clarify the mechanism have been extensively performed, especially for the glass transition temperature \(T_g\) of ultrathin films,\(^2-7\) confined liquids in nanopores,\(^8,9\) spheres,\(^10\) phase separated polymers,\(^11\) etc., but it still seems to be a controversial issue. \(T_g\) depends on various factors including size, status of the interface, geometry, and experimental method (sample preparation and observation). It is also noticeable that some systems show very weak or no size-dependence of \(T_g\) even below 100 nm.\(^6,7,10-12\)

On the other hand, researchers have been trying to understand the mechanism of glass transition in terms of cooperatively rearranging region (CRR),\(^13,14\) of which the size increases with decreasing temperature toward an underlying thermodynamic transition point leading to a drastic increase in relaxation time. The segmental relaxation time is supposed to be a function of the configurational entropy of the smallest CRR \(s_c^*\). The random first order transition (RFOT) theory,\(^15\) which has been developed recently, also supposes the existence of CRR, where nucleation for a transition in CRR is treated based on a mean field assumption. According to this theory, \(s_c^*\) depends on temperature, and the relaxation time depends on the configurational entropy per segment, size of CRR, distribution of relaxation times, dynamic fragility, and heat capacity difference between the glassy and liquid states. It is crucial how these parameters are affected by the various factors that alter \(T_g\) in nano-sized polymers in order to understand their anomalous glass transition dynamics.

We have been studying glass transition behaviors of ultrathin polymer shells deposited onto the surface of rod-like CaCO\(_3\) particles (whisker), and have found no \(T_g\) deviation from the bulk for both polystyrene and PMMA shells without crosslinking.\(^12\) This is also the case for their hollow shells. This seems to be quite inconsistent with the behaviors of ultrathin polymer films reported in the literature.\(^2-5\) On the other hand, for crosslinked polystyrene shells, enhanced \(T_g\)s from the bulk value have been observed depending on the shell thickness.\(^16,17\) This has been attributed to the heterogeneous nature of crosslink and also to unstable configurational structure retained by the crosslink. To elucidate further the dynamics and mechanism of the glass transition in the
thin shells of rod-like capsules, shells of various other polymers should be investigated.

In this paper, we investigate the glass transition behaviors of PMMA thin shells deposited on the surface of calcium carbonate whisker with different thicknesses and degrees of crosslink by temperature-modulated differential scanning calorimetry (TMDSC), and we compare their glass transition behaviors with those of polystyrene shells that we studied previously.\textsuperscript{16,17} To this end, we have prepared the PMMA capsules by two different methods, i.e., by radical polymerization in aqueous suspension of the whisker particles and by simple adsorption during bulk polymerization under dispersion of whisker particles. The latter method gives shells thinner than 10 nm.

**EXPERIMENTAL**

*Sample preparation*

Calcium carbonate whisker was supplied from Maruo Calcium Co. Methyl methacrylate (MMA) and the crosslink monomer, ethylene glycol dimethacrylate (EGDMA) were distilled under reduced pressure before use. Encapsulation of the calcium carbonate core was done by the following two methods; (1) radical polymerization in aqueous suspension of the whisker, and (2) adsorption of PMMA layer during bulk polymerization under dispersion of whisker particles (referred to as the adsorption method hereafter). Detailed description for the method (1) is presented in the previous papers.\textsuperscript{12,16} Co-polymerization of MMA/EGDMA was executed in aqueous suspension of CaCO\textsubscript{3} whisker particles stabilized by laurylbenzenesulfonic acid sodium salt. In the method (2), PMMA shell was deposited during bulk polymerization via simple physical adsorption. This method was applicable only to preparation of non-crosslinked shell because crosslink prevents the formation of thin layer due to apparent gelation. Atom transfer radical polymerization (ATRP) of MMA was done\textsuperscript{18,19} as follows: CaCO\textsubscript{3} whisker particles (400 mg) were suspended in MMA (10.0 g), and ethyl 2-bromoisobutyrate (6.4 mg), dinonyl-2,2’-bipyridine (138 mg), and Cu(I)Cl (16.0 mg) were added to this suspension. Then, it was immediately degassed under high vacuum. The reaction tube was sealed off after several freeze-pump-thaw cycles. The radical polymerization was executed at room temperature for 96 h. THF (200 mL) were added to the reacted mixture and the whisker particles were separated by centrifugation, washed with methanol several times, and finally dried under vacuum at 40°C for 24 h. On the other hand, the remaining PMMA/THF solution that contains no whisker was subject to precipitation in \textit{n}-hexane three times, and the obtained bulk PMMA was dried under vacuum at 60°C for 24 h. Molecular weight of this bulk PMMA was evaluated by size exclusion chromatography to be $M_n = 156$ kg mol\textsuperscript{-1}, and $M_w = 214$ kg mol\textsuperscript{-1}.\textsuperscript{18,19}
Hollow samples were also prepared from the core/shell capsules obtained above (filled capsules) by simply dissolving the inorganic core in hydrochloric acid. All the prepared capsules were washed with methanol and were dried under vacuum for 170 h at room temperature before the DSC measurements were taken. In this study, we define the degree of crosslink $X_c$ as

$$X_c = \frac{m_{\text{EGDMA}}}{(m_{\text{MMA}} + m_{\text{EGDMA}})}$$

where $m_{\text{MMA}}$ and $m_{\text{EGDMA}}$ are the masses of MMA and EGDMA fed in the reaction mixture.

Reference bulk samples were prepared from the hollow particles: hollow samples were first dissolved in THF, followed by drying (casting) at room temperature. The yielded bulk films were further dried in vacuum at 60ºC for 168 h.

Morphology of the obtained capsules was examined by transmission electron microscopy (TEM) by use of a Joel JEM-2100 (200 kV). The average shell thickness and its standard deviation were evaluated from TEM micrographs by measuring at hundreds of different locations of different particles.

**Calorimetry**

Glass transition behaviors were investigated by using a Perkin-Elmer Pyris Diamond DSC calorimeter. TMDSC measurements were performed: a saw-tooth modulation with amplitude of 0.5 K and a period of 60 s was superimposed on a cooling scan at $-0.2$ K min$^{-1}$, which started at a temperature well above $T_g$ (typically ca. 140ºC). The Lissajous plots showed negligible non-linear effect of thermal response. To evaluate the heat capacity data around $T_g$, we performed step-scan DSC measurements: each step consisted of a heating stage of 2 K at 5.0 K min$^{-1}$ followed by a temperature holding segment for 1.5 min. Complex heat capacity was evaluated from the heat flow data of TMDSC for each modulation cycle, and the storage and loss heat capacities ($C'$ and $C''$, respectively) were obtained with respect to temperature. The characteristic length at the glass transition $\xi(T_g)$ was evaluated from the loss heat capacity trace $C''(\omega)$ according to the fluctuation-dissipation theory. We used literature values of heat capacity for the evaluation of $\Delta(1/C_V)$ that was needed to obtain the values of $\xi(T_g)$. Detailed method of evaluation is described in the previous paper. To evaluate the standard deviation for the obtained data, we performed multiple measurements (3 – 10 times) for each DSC scan with different specimens. We also found that the loss of sample mass after each DSC scan does not exceed 0.2% of the polymer mass. As for the hollow capsules, we could not obtain reliable data for $\xi(T_g)$ because the hollow structure collapsed to some extent after the TMDSC scan. Therefore, in this paper, we present only the $T_g$ values obtained by the step-scan measurements for the hollow samples. In contrast, the filled
capsules were rather stable: they did not exhibit apparent morphological change as observed by the TEM after the TMDSC scan, and a few succeeding TMDSC scans gave almost identical results.

Estimation of interfacial tension

Interfacial tension $\gamma_{SL}$ for PMMA and polystyrene (for comparison) on the CaCO$_3$ surface was evaluated by the procedure based on the Fowkes-van Oss-Chaundhury-Good method. CaCO$_3$ whisker was pressed at 100 kg cm$^{-2}$ for 10 min with degassing to make a pellet with a specular surface. Water, glycerol, and ethylene glycol were employed as probe liquids. Contact angle for the droplet on the CaCO$_3$ pellet surface for the above three liquids was measured, and the surface tension parameters for CaCO$_3$ were evaluated by use of the literature values for the three liquids. Using also the literature values for the surface tension parameters for the polymers we evaluated $\gamma_{SL}$ for PMMA/CaCO$_3$ and polystyrene/CaCO$_3$ as

$$\gamma_{SL} = (\sqrt{\gamma_{SW}^{LW}} - \sqrt{\gamma_{LW}^{LW}})^2 + 2(\sqrt{\gamma_{S}^{S} \gamma_{S}^{L}} + \sqrt{\gamma_{L}^{S} \gamma_{L}^{L}} - \sqrt{\gamma_{S}^{S} \gamma_{L}^{L}} - \sqrt{\gamma_{S}^{L} \gamma_{S}^{L}})$$

(2)

where $\gamma_{LW}^{LW}$ is the Lifshitz-van der Waals component of the interfacial tension, $\gamma^+$ and $\gamma^-$ are the hydrogen bonding components, and the subscripts S and L denote solid and liquid, respectively.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows TEM images of the capsules prepared by the suspension polymerization. We see that the outer shells are successfully formed for various $X_c$s. We infer that in the suspension polymerization, a thin monomer layer is first formed onto the surface of whisker particles, then, radical polymerization proceeds in the layer as formed, which results in a polymer shell with a smooth surface. On the other hand, polystyrene shells prepared by a similar method exhibit relatively ragged surface compared with the PMMA shells, and under certain preparation conditions, a lot of spheres are attached to the whisker surface. This is probably due to higher interfacial energy at the layer/whisker for the polystyrene system. In this case, formation of spherical micell tends to be favored rather than that of unstable layer on the whisker surface. Contact angle measurements showed that an MMA/PMMA solution (7/3 by weight) exhibits higher wettability on CaCO$_3$ substrate than a styrene/polystyrene solution. This supports the above assumption. Detailed mechanism of radical polymerization of different monomers in the presence of suspended whisker particles
will be discussed in a separate paper on the basis of polymerization rate. The adsorption method also yielded core/shell capsules as shown in Figure 2, though the surface of the outer layer is thinner but less smooth than that from the suspension polymerization.

In the suspension polymerization method, the shell thickness can be controlled by the amount of monomer fed as was reported for polystyrene capsules.\textsuperscript{16,17} The thickness of the outer PMMA shells used in this study is shown in Table I.

Hollow capsules were successfully obtained from the samples prepared by the suspension polymerization method as shown in Figure 1 (b). However, from the sample prepared by the adsorption method, no rodlike hollow capsule was yielded. It is likely that fragmentation of the shell occurred in the acid treatment. This suggests less surface coverage by the shell from the adsorption method than from the suspension polymerization method. We also note from Table I that the shell thickness \(d\) increases after removing the core. This tendency is generally observed for the capsules prepared by the suspension polymerization. The as-polymerized shell is probably in an unstable configurational state, and thus structural relaxation occurs on removing the core, which results in the shell thickening.\textsuperscript{16} It is also noted that the thickening tendency is prominent for thinner shells. As for the thickest shell \((d = 93\text{ nm})\), on the other hand, the thickness does not change within the error range; the effect of unstable structure may be weakened for thicker shells.

**Glass transition behavior**

Figure 3 shows typical traces obtained from TMDSC cooling scan. The profile of \(C''(T)\), which exhibits a peak in the glass transition range, was fitted with a Gaussian function to evaluate the dynamic length scale \(\zeta(T_g)\). Figure 4 (a) shows the \(T_g\) difference between the non-crosslinked filled shell and the corresponding bulk, \(\Delta T_g = T_g^f - T_g^b\) plotted against the shell thickness \(d\). The result shows no \(T_g\) difference from the bulk for \(d \geq 23\text{ nm}\), while the shell with \(d = 8\text{ nm}\) exhibits lower \(T_g\) than the bulk. These results are in contrast to the reported \(T_g\) behavior of PMMA ultrathin films: PMMA films with \(d = \text{ca. 20 nm}\) on SiO\(_x\) substrates have been reported to exhibit \(T_g\) shifts of 5 – 10 K.\textsuperscript{26} On the other hand, no \(T_g\) shift has also been observed for non-crosslinked polystyrene shells,\textsuperscript{16} which is again in contradistinction from the drastic \(T_g\) shifts observed for ultrathin polystyrene films.\textsuperscript{2-5}

Figure 4 (b) shows ratio of the characteristic length scale of the non-crosslinked filled shell to that of the corresponding bulk \([\zeta(T_g)^f / \zeta(T_g)^b]\) plotted against \(d\). Here again, no distinct difference in \(\zeta(T_g)\) from the bulk is observed, though slight depression from the bulk may be discernible as a whole. The origin of this slight depression is not
clear. As for the filled capsules, the polymer content is small compared with the core, resulting in very weak $T_g$ signal. This might lead to unknown artifact in the data analysis. Anyhow, it is concluded that the glass transition dynamics of the non-crosslinked filled shells does not differ significantly from that in the bulk for $d \geq \text{ca. } 20 \text{ nm}$.

As for the thinnest shell (8 nm), $T_g$ is about 10 K lower than the bulk value, and $\xi(T_g)$ is slightly lowered (Figure 4). The origin of this $T_g$ depression is not clear, but it is probably related to the same mechanism as that in ultrathin films (surface/interface and confinement effects). The radius of gyration for the PMMA material of the thinnest shell (8 nm) is estimated to be 10.5 nm in the bulk state, which exceeds the shell thickness. This might result in unstable configuration in the shell. In addition, the difference in the shell formation process may affect the resulted configuration. In the case of spin-casting, for example, strong shear is expected to be imposed on the polymer, which may cause unstable polymer configurations. In the present deposition method, the shell is formed by simple adsorption, which is followed by evaporation of the residual monomer. Although the evaporation occurs gradually, the resulted polymer layer might be far from equilibrium state: at the late stage of casting, relaxation time becomes so large at a temperature well below $T_g$ that an equilibrium state is hard to be reached. Anyhow, it is indisputable that the present PMMA rod-like capsules as well as the polystyrene shells are less sensitive to the size effects on both $T_g$ and $\xi(T_g)$ than for ultrathin films. Similarly, weak or no size dependence has been observed for some other systems. Polystyrene microspheres exhibit no $T_g$ shift down to 40 nm in diameter in contradistinction from free-standing films. Ultrathin films of polysulfone exhibits no size dependence of $T_g$ down to 10 nm, and styrene-isobutylene block copolymer shows weak size dependence. As for the latter, the observed $T_g$ variation has been attributed to diffuse interface.

Figure 5 shows $T_g$ and $\xi(T_g)$ for the shells with similar thicknesses (17 – 23 nm) with respect to the degree of crosslink $X_c$. $T_g$ increases and $\xi(T_g)$ decreases with increasing $X_c$. The latter seems to be a general trend. Reduction of $\xi(T_g)$ with crosslink corresponds to broadening of the glass transition temperature range (we have confirmed this point experimentally). The observed reduction of $\xi(T_g)$ with respect to $X_c$ may be attributed to the heterogeneity that arises from crosslink, as well as to the reduced configurational entropy that is essential to crosslinked structure. It is reasonable to assume that segments near a crosslink point have lower mobility than those sufficiently separated from crosslink points. In addition, heterogeneity in spatial distribution of the crosslink points may be responsible for the $T_g$ broadening: as far as the difference in the reactivity of polymerization between MMA and EGDMA exists, localization of the crosslink
points occurs to some extent, though we cannot characterize this feature quantitatively at present.

In Figure 5, we observe no significant difference between the filled shell and the corresponding bulk for both $T_g$ and $\zeta(T_g)$. This is contrastive to the result of polystyrene rodlike shells where $T_g$ increases from the bulk value as the degree of crosslink increases.$^{17}$ This $X_c$ dependence for the polystyrene shells has been explained as follows: crosslink tends to retain unstable configuration that were established during the shell formation, while for non-crosslinked shells, the unstable configuration can readily relax to a bulk-like one during the DSC scan. Thus, we infer that in the present PMMA shells fairly stable configuration may have already been formed during the suspension polymerization. This may be related to the polymerization mechanism: as mentioned before, MMA is more compatible (high wettability) with the CaCO$_3$ surface than styrene, which results in a relatively stable MMA layer on the whisker surface in the suspended state. It has been argued that the $T_g$ shift of ultrathin films depends on the interfacial tension of polymer/substrate,$^{24}$ though the density near the interface should also be taken into account to describe the interfacial effect.$^{29}$ We evaluated the interfacial tension $\gamma_{SL}$ for PMMA/CaCO$_3$ and polystyrene/CaCO$_3$ to be 1.5 and 2.1 mJ m$^{-2}$, respectively. The $T_g$ shift observed for crosslinked polystyrene shells may be due to the higher interfacial tension for polystyrene/CaCO$_3$ that leads to lower stability of the as-attached shell.

Alternatively, no $T_g$ shift for the crosslinked PMMA shells may be attributed to an essential nature of the material that $T_g$ is relatively insensitive to the size. For ultrathin films, in general, thickness dependence of $T_g$ varies prominently with the chemistry of polymer. It has been generally reported that the thickness dependence of $T_g$ is stronger for polystyrene films than for PMMA films,$^{2,26}$ and that for films of poly(vinyl acetate) with absorbed water no $T_g$ shift is observed even for $d = 23$ nm.$^{30}$ Recent theoretical studies claim that the fragility of polymers should have a negative correlation with packing efficiency that is governed by the shape of monomer unit.$^{31,32}$ PMMA has a flexible side group compared with polystyrene, which may result in higher packing efficiency. Riggleman et al assume that the fragility is reduced in highly confined systems such as in ultrathin polymer films.$^{33}$ According to this hypothesis, the confinement effect on the fragility is expected to be weaker for stronger liquids because of their low fragility even in the original bulk state. Assuming that the size dependence of fragility is correlated to that of $T_g$, we speculate that the size dependence of $T_g$ is greater for polymers with higher fragility. Unfortunately however, the reported values of the Angell’s dynamic fragility parameter $m$ for PMMA and polystyrene do not confirm
Table II shows the glass transition temperatures obtained from the step-scan measurements for the filled and hollow shells. Little difference in $T_g$ between the filled and hollow shells is observed. Considering the little size dependence of $T_g$ for the filled shell with $d \geq ca. 20$ nm, this result may be reasonable (the hollow shell is generally thicker than the filled shell) despite that the status of the interface is quite different.

Figure 6 shows $\xi(T_g)$ plotted against $T_g$ for various PMMA samples containing filled capsules with various $X_c$ and $d$, and bulk samples. $\xi(T_g)$ largely decreases with increasing $T_g$, though considerable dispersion of the data is observed. Additionally, the shell with $d = 8$ nm does not obey the universal trend as indicated by an arrow in Figure 6. This is probably due to the different mechanism of shell formation in the adsorption method as discussed before. For comparison, the data for the crosslinked polystyrene system including bulk samples are also shown in Figure 6, which exhibit a clearer decreasing feature of $\xi(T_g)$ with respect to $T_g$, revealing a single universal curve.

It has been demonstrated experimentally that in glass formers, dynamic heterogeneity exists without any static (structural) correlations, and the length scale of this dynamic heterogeneity increases as temperature approaches $T_g$. It is pertinent to consider that the present length scale $\xi(T_g)$ estimated by TMDSC corresponds to such length scale of dynamics heterogeneity. If we assume that $\xi(T_g)$ corresponds to the size of CRR of the Adam-Gibbs model, the decrease in $\xi(T_g)$ with increasing $T_g$ shown in Figure 6 implies that the segmental relaxation time $\tau$ is not a unique function of the size of CRR. In other words, the same absolute value of $\tau$, which is typically $10^2 – 10^3$ s at $T_g$, can be associated with different size of CRR depending upon the degree of crosslink, shell thickness, status of interface, etc.

As for the PMMA system, $T_g$ variation is actually due to variation of $X_c$, because $T_g$ is almost independent of the shell thickness and of the status of interface except for the thinnest (8 nm) shell. Thus, the trend in Figure 6 implies that the higher the density of crosslink, the smaller becomes the CRR at $T_g$. This may be reasonably understood: when crosslink occurs, the CRR at $T_g$ has to become smaller to keep the relaxation time as $\tau(T_g) = 10^2 – 10^3$ s. The slope of the profile, which actually represents $X_c$ dependence of $\xi(T_g)$ in the case of PMMA system, is considered to be manifestation of the crosslink effect on relaxation time. Linear regression analysis shown by the solid lines in Figure 6 reveals that the slope is greater for the polystyrene system than for the PMMA system. As for the polystyrene system, $\xi(T_g)$ depends not only on $X_c$ but also on shell thickness. However, the present results might show that the crosslink effect on segmental relaxation time is rather strong for the polystyrene system. This may be due to the stiff
feature of polystyrene chain in the amorphous state.

The results in Figure 6 also seem to be compatible with both the Adam-Gibbs and the RFOT theories.\textsuperscript{13,15} According to the Adam-Gibbs theory, \( \xi(T_g) \) can be written as

\[
\xi(T_g)^3 = \ln \left[ \frac{\tau(T_g) T_g}{\tau_0} \right] \frac{k T_g}{\Delta \mu}
\]

where \( \Delta \mu \) is the activation energy for cooperative rearrangement per unit volume, \( \tau_0 \) is the prefactor which determine the absolute value of relaxation time, and \( k \) is the Boltzmann constant. Given that the profile in Figure 6 is due to the crosslink effect, one can draw a quite reasonable conclusion that both \( \tau_0 \) and \( \Delta \mu \) increase with \( X_c \) under the condition that \( \tau(T_g) \) is constant. According to the recent argument based on the RFOT theory,\textsuperscript{37} on the other hand, \( \ln(\tau/\tau_0) \) is expressed by a universal increasing function \( F \) of the configurational entropy of a CRR as

\[
\ln \left[ \frac{\tau(T_g)}{\tau_0} \right] = F \left[ \frac{\xi(T_g)^3 S_c(T_g)}{k} \right]
\]

where \( S_c \) is the configurational entropy per unit volume, and thus, corresponds to the configurational entropy of a CRR. Considering that both \( \xi^3 \) and \( S_c \) decrease with increasing \( X_c \), the prefactor \( \tau_0 \) should increase with \( X_c \).

CONCLUSIONS

In this study, we have successfully synthesized various rod-like capsules consisting of a calcium carbonate core and a PMMA-based polymer shell by the two methods, i.e., suspension polymerization, and the simple adsorption method. We have investigated glass transition dynamics of the obtained thin PMMA shells by use of TMDSC technique, and have revealed the following points:

(1) For non-crosslinked shells of \( d \geq 23 \) nm, \( T_g \) and \( \xi(T_g) \) are approximately the same as those of the bulk samples, being independent of the shell thickness.

(2) Non-crosslinked shell with \( d = 8 \) nm shows a reduced \( T_g \) from the bulk value. The result may be attributed to the different mechanism of shell formation as well as to the very small value of \( d \).

(3) Crosslinked PMMA shells do not show \( T_g \) deviation from the bulk up to \( X_c = 7.0\% \). This is in contrast to the results for the polystyrene shells. The result may be attributed to different stability of the shell as revealed by the difference in interfacial energy, and/or to the different feature of segment packing that arises from the chemical structure.
(4) Hollow shells exhibit neither $T_g$ nor $\xi(T_g)$ shift from the bulk for $d \geq$ ca. 20 nm.

(5) $\xi(T_g)$ exhibits a universal profile that decreases with increasing $T_g$. This may be interpreted as the crosslink effect on the size of CRR at $T_g$.

ACKNOWLEDGEMENTS

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Table I. Thickness of outer PMMA shells

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<th>Sample</th>
<th>$X_c$ (wt%)</th>
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<th>Hollow</th>
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<td>A</td>
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<td>8 ± 1</td>
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</tr>
<tr>
<td>B</td>
<td>0</td>
<td>23 ± 5</td>
<td>50 ± 8</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
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<td>65 ± 9</td>
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<tr>
<td>D</td>
<td>0</td>
<td>93 ± 19</td>
<td>79 ± 8</td>
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</tr>
<tr>
<td>G</td>
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Table II. Glass transition temperature obtained from DSC step-scan heating

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<th>Sample</th>
<th>$X_c$ (wt%)</th>
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<td>B</td>
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<tr>
<td>H</td>
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<td>403.7 ± 0.7</td>
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FIGURE CAPTIONS

**Figure 1.** Electron micrographs of (a) non-crosslinked filled capsule, (b) non-crosslinked hollow capsule, (c) non-crosslinked filled capsule with a thicker shell \( d = 93 \text{ nm} \), (d) filled capsule with \( X_c = 1.0\text{wt\%} \), (e) filled capsule with \( X_c = 3.0\text{wt\%} \), and (f) filled capsule with \( X_c = 7.0\text{wt\%} \).

**Figure 2.** Electron micrographs of non-crosslinked filled capsule with \( d = 8 \text{ nm} \) prepared by the adsorption method.

**Figure 3.** Typical traces for \( C' \) and \( C'' \) obtained by TMDSC cooling scan for non-crosslinked filled shells with different thicknesses. The fitted Gaussian curve for \( C''(T) \) is also presented by the solid curves.

**Figure 4.** Deviation of \( T_g \) from the bulk \( \Delta T_g = T_g^f - T_g^b \) and the ratio \( \zeta(T_g)^f / \zeta(T_g)^b \) for non-crosslinked filled shells plotted against shell thickness \( d \).

**Figure 5.** \( T_g \) and \( \zeta(T_g) \) plotted against \( X_c \) for filled shells and the bulk samples.

**Figure 6.** \( \zeta(T_g) \) plotted against \( T_g \) for PMMA and polystyrene systems. The data include filled capsules and bulk samples. The solid lines indicate results of linear regression analysis.
GRAPHICAL ABSTRACT
Rodlike capsules consisting of a calcium carbonate core and a thin poly(methyl methacrylate) shell were synthesized. For the polymer shells thicker than 20 nm, $T_g$ is not altered from the bulk value, while a shell of 8 nm thick exhibits a lowered $T_g$ from the bulk, but the length scale of dynamic heterogeneity $\zeta(T_g)$ exhibits no distinct dependence on $d$. Correlation between $\zeta(T_g)$ and $T_g$ was revealed, which is interpreted in terms of the concept of cooperatively rearranging region.