ORIGINAL ARTICLE

Preparation and glass transition of crosslinked poly(vinyl acetate) thin shells on the surface of a calcium carbonate core

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Rod-like capsules consisting of a thin poly(vinyl acetate) (PVAc) shell and a calcium carbonate core were synthesized by suspension polymerization. Thin shells of crosslinked PVAc were successfully made with thicknesses ranging from 12 to 19 nm, whereas no core/shell capsules were obtained without crosslinking, suggesting that crosslinking has an important role in the stabilization of the deposited shell. The shell thickness was independent of the relative amount of fed monomer, unlike the polystyrene and poly(methyl methacrylate) (PMMA) systems. The glass transition temperature, T_g , and the dynamic length scale, $\xi(T_g)$, for the deposited PVAc shells were evaluated using temperature-modulated differential scanning calorimetry. The T_g and $\xi(T_g)$ of the filled shells were higher and lower, respectively, than the bulk values. The results are compared with those of polystyrene and PMMA shells, and are discussed in terms of the surface/interface and configuration effects. The T_g shift observed in the present shells may be partly attributed to an unstable configuration that is retained by the crosslinks.

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INTRODUCTION

Techniques for preparing nanosized capsules made of various polymeric materials used in nanotechnology and pharmaceuticals have been developed. Encapsulation techniques that take advantage of the self-assembly of amphiphilic molecules, such as micelles and vesicles, have been extensively studied, and those using a core particle as a template have also been developed.^{1–3} The latter techniques involve layer-by-layer deposition, solvent evaporation and emulsion polymerization.^{1,4,5} Recent developments in nanotechnology have attracted significant attention in the polymer physics community to the anomalous dynamics (especially the glass transition dynamics) characteristic of nanosized or nanoconfined systems.^{6,7}

In particular, the glass transition behaviors of ultrathin films, where the glass transition temperature, T_g , deviates from that of the bulk polymer depending on the film thickness, substrate and preparation conditions are of interest; some of the experimental results are controversial.^{6,8–10} The observed T_g shift is assumed to be caused by various factors, such as the surface/interface region, polymer chain confinement and non-equilibrium configurations induced during the film preparation. These factors may interact with one another, increasing the complexity of the mechanism that is not yet fully understood. In addition, the size effect on T_g has been studied for systems with geometries other than thin film, for example, polymer spheres,^{11,12} microphase-separated systems¹³ and glass-forming

liquids confined in nanopores.⁶ In general, the observed T_g behaviors for such systems do not necessarily coincide qualitatively with those of thin films, suggesting certain geometry effects on the T_g in nanosized materials.

We have previously investigated the preparation and thermal properties of rod-like capsules that consist of a polymer thin shell and a rod-like calcium carbonate core with shell thicknesses of 8–130 nm.^{14–17} These capsules generally show T_g behaviors different from those of flat thin films. For example, non-crosslinked polystyrene thin shells show no T_g deviation, whereas the T_g of crosslinked polystyrene shells is higher than that of bulk polystyrene. Furthermore, the T_g of poly(methyl methacrylate) PMMA shells show a subtle size dependence. These results suggest again that the mechanism of the T_g deviation in nanosized systems is rather complex. It is important to conduct glass transition studies of rod-like core/shell capsules for a broader range of polymer materials. However, the broadening of the range of materials is limited by the sample preparation technique.

We have already reported that the suspension polymerization technique can produce capsules for synthetic vinyl polymers, such as polystyrene, PMMA and poly(hydroxyethyl methacrylate).¹⁴ However, capsules with a poly(vinyl acetate) (PVAc) shell have not previously been obtained using this technique, probably owing to the instability of thin shells of PVAc. Crosslinking is expected to be an effective technique to stabilize the PVAc thin shell. We have reported

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that polystyrene shells can be stabilized by crosslinking via copolymerization with divinylbenzene,¹⁵ and that chitosan shells prepared by a deposition method can be stabilized by crosslinking using diisocyanate compounds.¹⁸

In this work, we successfully prepared rod-like capsules possessing a PVAc shell by introducing crosslinks. We used triallyl isocyanurate as a crosslinking reagent that possesses three reactive allyl groups. We investigated the glass transition behavior of the crosslinked PVAc shells by using temperature-modulated differential scanning calorimetry (TMDSC) and discuss the dynamics of these nano-sized polymers in comparison with those of polystyrene and PMMA thin shells.

EXPERIMENTAL PROCEDURE

Preparation of capsules

The preparation of capsules with a crosslinked PVAc shell was performed via free radical polymerization in an aqueous suspension.¹⁴ Vinyl acetate (monomer) from Wako Pure Chemicals Industry, Osaka, Japan, was distilled before use. Triallyl isocyanurate (crosslinking reagent) and lauryl benzenesulfonic acid sodium salt (surfactant) were purchased from Tokyo Chemical Industry, Tokyo, Japan. Calcium carbonate rod-like whiskers with diameters between 300 and 600 nm and lengths between 1.0 and 3.0 μm were supplied by Maruo Calcium, Akashi, Japan. Nonylphenyl polyethylene glycol (surfactant) was supplied by the NDF Corporation, Tokyo, Japan. For a typical polymerization, calcium carbonate whiskers (4.0 g), vinyl acetate (2.0 g), triallyl isocyanurate (40 mg), lauryl benzenesulfonic acid sodium salt (180 mg) and nonylphenyl polyethylene glycol (8 mg) were added to distilled water (67 ml), and a well-suspended state was achieved by sonication. An aqueous solution of 10 wt% potassium peroxodisulfate (5 ml) was added to the suspension slowly for about 120 min while stirring at 350 r.p.m. under a nitrogen atmosphere at 333 K. The suspension was stirred for an additional 8 h at 333 K until the monomer was largely exhausted. The precipitate was separated at room temperature and was washed with *n*-hexane several times to remove the surfactants and unreacted monomer. The obtained powder was further washed with methanol to remove the spherical particles formed by polymerization in spherical micelles. The sample was added to distilled water, the microspheres were extracted as a suspension in water by sonication and then the precipitate (rod-like particles) was separated by filtration. This procedure was repeated several times. Finally, the separated rod-like particles were dried under vacuum for 24 h at 303 K.

Reference bulk samples with each degree of crosslinking (X_c) were prepared from the corresponding capsules. The core/shell capsule was ground into fine powder and added to hydrochloric acid (3.5 wt%) to remove the core material (calcium carbonate). The insoluble precipitate (polymer) was separated by filtration and dissolved in tetrahydrofuran. The solution was dried in atmosphere and further dried under vacuum for 24 h at 303 K to obtain a bulk cast film.

Because we could not determine the actual extent of crosslinking in the prepared shell, X_c is estimated as the mass fraction of the crosslinking reagent fed in the reaction,

$$X_c = m_{\text{TI}} / (m_{\text{VAc}} + m_{\text{TI}}), \quad (1)$$

where m_{VAc} and m_{TI} are the masses of vinyl acetate and triallyl isocyanurate, respectively. We performed the polymerization with $X_c = 0$ –5.0%, which corresponds to 0.35–1.79 mol% of triallyl isocyanurate.

Characterization

The morphology of the capsules was examined by transmission electron microscopy (TEM) by using a Jeol JEM-2100TM microscope operated at 200 kV (Jeol, Akishima, Japan). The thickness of the polymer shell and its standard deviation were evaluated from TEM micrographs by measuring at hundreds of different locations on different particles. To evaluate the core/shell ratio, thermogravimetric analysis (TGA) was performed using a Shimadzu DTG-60/60H thermogravimetric analyzer (Shimadzu, Kyoto, Japan); the samples were heated to 873 K at 20 K min⁻¹ in air. The polymer mass content was

determined from the weight loss after the scan. We calculated the hypothetical shell thickness, d_{TGA} , assuming a simple rod model for the core,

$$d_{\text{TGA}} = \frac{\alpha_{\text{loss}} r L d_c}{2(r+L)(1-\alpha_{\text{loss}})d_p}, \quad (2)$$

where r and L are the radius and length of the rod-like core, respectively, d_c and d_p are the density of the core and the polymer, respectively, and α_{loss} is the polymer content obtained from TGA measurements, such that

$$\alpha_{\text{loss}} = \frac{m_{\text{polymer}}}{m_{\text{core}} + m_{\text{polymer}}}. \quad (3)$$

Here, we used $r = 225$ nm, $L = 1500$ nm, $d_c = 2.711$ g cm⁻³, and $d_p = 1.19$ g cm⁻³. The interfacial free energy for PVAc/CaCO₃ was evaluated by a procedure based on the Fowkes-van Oss-Chaudhury-Good method.^{19–21} We used a literature value of 36.5 mJ m⁻² for the surface tension of PVAc²² and a previously obtained value of 53.6 mJ m⁻² for that of CaCO₃.¹⁷ The procedure is described elsewhere.¹⁷

Calorimetry

The glass transition dynamics of the polymer shell was characterized by the TMDSC. We used a Perkin–Elmer Pyris Diamond DSC calorimeter equipped with a Perkin–Elmer Intra-cooler P2 cooling system (Perkin–Elmer, Waltham, MA, USA). The temperature and heat flow were calibrated with an indium standard, and the measurements were performed under a nitrogen atmosphere. For the measurements of the filled shells, the glass transition signal is very weak because of the low polymer content. Therefore, we used large volume capsules (Perkin–Elmer 0319-0218) with typical sample sizes of 50–60 mg. The temperature shift due to this large sample size was examined by measuring the T_g of the bulk polymer mixed with the CaCO₃ whiskers. The difference in the T_g from that of the normal sample size was within the s.d. estimated via multiple measurements. In the TMDSC measurements, a sawtooth modulation with an amplitude of 0.5 K and a period of 60 s was superimposed on a cooling scan at -0.2 K min⁻¹, starting at 343 K (well above the calorimetric T_g of the samples). Multiple TMDSC scans were performed on different specimens of each sample to estimate the standard deviations of the T_g and the dynamic length scale, ξ . The absolute values of heat capacity, $C_p(T)$, required for the evaluation of the ξ at T_g , $\xi(T_g)$, were obtained from the literature.²³ By Fourier transformation of the TMDSC heat flow data, we evaluated T_g and $\xi(T_g)$, based on the fluctuation–dissipation theory.²⁴ The details are described elsewhere.¹⁶

RESULTS AND DISCUSSION

Morphology

Figure 1 shows electron micrographs of the core/shell capsules with crosslinked PVAc shells. The PVAc shell successfully formed on the surface of the whiskers, although the thickness appears to be very thin. The existence of the shell is more clearly seen in the end part of the rod-like capsules, where the core material was partly lost (Figures 1a, b and d). Such partial loss of the core is occasionally observed; we infer that the loss occurred during the purification (stirring) process after polymerization.

The thickness determined from TEM, d_{TEM} , is listed in Table 1. We tried to control the thickness by varying the relative amount of monomer fed during polymerization (the mass ratio of monomer to core, $m_{\text{m}}/m_{\text{core}}$). However, d_{TEM} was not considerably altered by varying $m_{\text{m}}/m_{\text{core}}$; in contrast, the d_{TEM} values of polystyrene and PMMA shells increase with increasing $m_{\text{m}}/m_{\text{core}}$.^{15,17}

We tried to prepare hollow capsules by acid treatment; the core/shell capsule was immersed in hydrochloric acid to remove the core, and the precipitate was separated. However, only shell debris (no hollow capsules) was found by TEM observation. The micrographs in Figure 1 show that the surface of the deposited shell is rather ragged, suggesting that the crosslinked shell is brittle and not uniform. It is important to note that non-crosslinked PVAc shells cannot be obtained by this

Figure 1 Transmission electron micrographs of core/shell capsules: (a) degree of crosslinking (X_c)=1.0%, m_m/m_{core} =0.5, (b) X_c =2.0%, m_m/m_{core} =0.5, (c) X_c =5.0%, m_m/m_{core} =0.5, (d) X_c =2.0%, m_m/m_{core} =1.5, (e) X_c =2.0%, m_m/m_{core} =2.5 and (f) X_c =5.0%, m_m/m_{core} =2.5.

polymerization technique, reflecting the instability of thin PVAc shell itself. Crosslinking is thought to raise the T_g and improve the shell stability. We were able to obtain hollow capsules from capsules with a higher degree of crosslinking (X_c =10%), as shown in Figure 2. However, numerous inseparable sphere particles also formed that aggregated and coalesced on the shell surface. The tendency of spheres to aggregate was stronger for higher degrees of crosslinking.

TEM observation indicates that, in general, spherical PVAc particles are produced in addition to the shell, and that the number of spheres tends to increase with increasing m_m/m_{core} , as shown in Figure 1f.

The diameters of the spheres, likely formed via suspension polymerization or emulsion polymerization in spherical micelles, ranged from 60 to 120 nm. The increase in sphere amount for a larger m_m/m_{core} is reflected in the d_{TGA} values in Table 1. The difference between d_{TGA} and d_{TEM} is significant for a higher m_m/m_{core} . The number of polymer spheres likely increases as the amount of monomer increases, whereas the shell thickness remains constant. After polymerization, the capsules were washed with methanol several times and separated by membrane filtration. This methanol washing effectively removes the small spheres. Although PVAc is soluble in methanol, the shell was not

removed from the core surface likely as a result of crosslinking. However, the spheres could not be completely removed from samples with high m_m/m_{core} . In such cases, the spheres aggregated and attached to the capsule surface, as shown in Figure 1f. Once aggregation has occurred, the spheres cannot be removed by the above procedure. By contrast, the spheres can be successfully removed from samples with a low m_m/m_{core} . In this case, d_{TGA} is approximately identical to d_{TEM} (Table 1).

We infer that the shell formation occurs mainly via bulk polymerization in a thin monomer layer deposited on the whisker surface that is stabilized by the surfactant. However, presenting this PVAc system, the shell surface is rather rough, and shell thickening with increasing m_m/m_{core} is not observed. On the contrary, the shells of PMMA/ $CaCO_3$ and polystyrene/ $CaCO_3$ capsules are more uniform and have a relatively smooth surface, and the shell thickness increases almost linearly with increasing m_m/m_{core} . These results suggest relatively low stability of the monomer layer during polymerization in the PVAc/ $CaCO_3$ system. Moreover, the solubility of vinyl acetate in water (2.3 wt%) is higher than that of styrene (0.04 wt%) and MMA (1.5 wt%), possibly preventing the formation of thick shells of PVAc.

Glass transition

Because we could not obtain hollow shells, the present calorimetric analysis is focused only on the filled shells. Here, we use two filled

Table 1 Shell thicknesses determined by TEM (d_{TEM}) and by TGA (d_{TGA})

Sample	X_c (%)	m_m/m_{core}	d_{TEM} (nm)	d_{TGA} (nm)
F1-1	1.0	0.5	12 ± 4	13.0
F2-1	2.0	0.5	16 ± 5	11.8
F2-2	2.0	1.5	19 ± 9	14.7
F2-3	2.0	2.5	14 ± 5	29.7
F5-1	5.0	0.5	16 ± 6	15.2
F5-2	5.0	1.5	14 ± 7	39.7
F5-3	5.0	2.5	15 ± 5	76.5

Abbreviations: d_{TGA} , shell thickness determined from TGA; d_{TEM} , thickness determined from TEM; m_m/m_{core} , the mass ratio of monomer to core; TGA, thermogravimetric analysis; TEM, transmission electron microscopy; X_c , degree of crosslinking.

Figure 2 Hollow crosslinked capsule with degree of crosslinking (X_c)=10% obtained by hydrochloric acid treatment.

samples, F2-1 and F5-1 in Table 1, that are suitable for glass transition analysis because d_{TEM} agrees with d_{TGA} within experimental error. We assume that the contribution of any spherical particles included in these samples is negligible. Because the mass fraction of PVAc is rather low (0.049–0.062), the glass transition signal for these samples is very subtle. To overcome this difficulty, we used large volume capsules and performed multiple measurements as described in the experimental section.

Figure 3 shows typical profiles for the storage and loss heat capacities, $C'(T)$ and $C''(T)$, respectively, which were obtained from TMDSC cooling scans. The $T_g(\omega)$ and $\xi(T_g)$ were determined using a fitting analysis with a Gaussian function ($\omega=1.05 \times 10^{-2} \text{ rad s}^{-1}$). The results are presented in Table 2. The filled shells have a higher T_g and a smaller $\xi(T_g)$ than the bulk polymer, although the T_g difference between the samples with $X_c=2.0$ and 5.0 wt% is not very large.

It has been reported that the T_g of PVAc is lowered by a small amount of water absorbed from the ambient atmosphere and that the T_g reaches an ultimate value (ca. 313 K) after annealing at 393 K for 5 h.²⁵ The T_g of spin-coated PVAc films saturated with water absorbed

Figure 3 Typical traces for storage and loss heat capacities (C') and (C''), respectively, obtained by temperature-modulated differential scanning calorimetry of (a) a crosslinked filled shell (F2-1) and (b) its corresponding bulk sample. The fitted Gaussian curves for C' are also presented.

Table 2 Parameters calculated from TMDSC measurements

Sample	X_c (%)	d_{TEM} (nm)	T_g (K) ^a	$\xi(T_g)$ (nm)
F2-1	2.0	16 ± 5	324.4 ± 1.0	1.9 ± 0.3
Bulk	2.0		316.5 ± 0.5	2.7 ± 0.1
F5-1	5.0	16 ± 6	325.4 ± 1.4	2.2 ± 0.3
Bulk	5.0		317.5 ± 0.2	2.6 ± 0.2

Abbreviations: d_{TEM} , thickness determined from TEM; m_m/m_{core} , the mass ratio of monomer to core; T_g , glass transition temperature; $\xi(T_g)$, dynamic length scale; TMDSC, temperature-modulated differential scanning calorimetry; X_c , degree of crosslinking.

^aObserved at $\omega=1.05 \times 10^{-2} \text{ rad s}^{-1}$.

from the atmosphere have no thickness dependence, at least for films thicker than 23 nm.²⁵ The present PVAc shells do not appear to be seriously affected by absorbed water because both the T_g and $\xi(T_g)$ are different from those of the bulk film (size effects are observed). In addition, the same drying process was used for the capsules and bulk samples (see the experimental section). It has also been reported that a spin-cast film as thick as 23 nm shows a T_g reduction of several K when the absorbed water is thoroughly removed.²⁵ Dielectric relaxation studies show somewhat contradictory results for PVAc thin films; Fukao *et al.*²⁶ have reported that the peak temperature (T_α) for the α -relaxation process (at 100 Hz) gradually decreases with decreasing thickness (d) for $d < 1 \mu\text{m}$, whereas Serghei *et al.*²⁷ found that T_α (at 38 Hz) is constant with respect to d down to 27 nm. Incidentally, in the latter case, a T_α reduction of just a few K is observed at $d=16$ nm. This discrepancy may be attributed not only to the difference in frequency but also to differences in the film surface (interface). In any case, these results show that the T_g of PVAc spin-cast films is generally lowered as the thickness decreases. In contrast, the present PVAc shells have a higher T_g than the bulk; the same trend is also observed for crosslinked polystyrene shells.¹⁶

The present PVAc shells have a lower $\xi(T_g)$ than the bulk, indicating a broadening of the glass transition range, that is, of the distribution of segmental relaxation times. It has been shown from dielectric relaxation studies on spin-cast films that the distribution of relaxation times is altered with respect to d : the modes at the slower end of the relaxation are frozen.²⁷ Although this does not necessarily mean broadening of the distribution of relaxation times, the distribution does depend on size, supporting the observed difference between the $\xi(T_g)$ of the PVAc shells and the corresponding bulk.

It should be noted that the crosslinking reagent used, triallyl isocyanurate, may result in a less ideal random network of PVAc than in the styrene/divinylbenzene or methyl methacrylate/ethylene glycol dimethacrylate systems. The reported reactivity ratio is $r_1=0.278$ (vinyl acetate) and $r_2=1.95$ (triallyl isocyanurate).²⁸ Indeed, there appear to be few crosslinking reagents that are suitable for homogeneous copolymerization with vinyl acetate, and triallyl isocyanurate remains one of the best reagents for crosslinking of PVAc to our knowledge. Considerable crosslink heterogeneity may further broaden the glass transition range. It would not, however, explain the difference between the $\xi(T_g)$ of the filled shell and the bulk polymer because the heterogeneous nature of the crosslinks is not altered by the conversion from a shell to a bulk sample (acid treatment and casting).

We now compare the results for PVAc thin shells with those for polystyrene and PMMA thin shells.^{16,17} Table 3 summarizes the general trends of the glass transition parameters for crosslinked filled shells. Here, $\Delta T_g = T_g^{\text{shell}} - T_g^{\text{bulk}}$ and $\Delta \xi(T_g) = \xi(T_g)^{\text{shell}} - \xi(T_g)^{\text{bulk}}$. The PVAc shell trends are the same as those of polystyrene. The T_g shift is larger for polystyrene shells than for PVAc shells; $\Delta T_g=17$ K for

a polystyrene shell with $d=20$ nm, whereas $\Delta T_g=8$ K for a PVAc shell with $d=16$ nm (F5-1).

Considerable evidence has been reported for the existence of an interfacial layer with a mobility different from that of the bulk,^{8,12,29–32} influencing the apparent T_g (spatially averaged T_g) of a nanomaterial as a whole. At a core/shell or polymer/substrate interface, the segmental mobility is frequently lowered by a strong interaction with the core material (or substrate), increasing the apparent T_g . Fryer *et al.*²¹ proposed that the T_g deviation is an increasing function of the interfacial free energy. The free energy at the core/shell interface was estimated to be 1.9 mJ m^{-2} for PVAc/ CaCO_3 , 1.5 mJ m^{-2} for PMMA/ CaCO_3 and 2.1 mJ m^{-2} for polystyrene/ CaCO_3 . The free energy values might explain the trend of ΔT_g in Table 3. However, it is claimed that the interfacial free energy is not a suitable parameter for interpreting the interfacial effect on T_g .³³ In addition, the free surface (polymer/air interface) effect, which may depend on the polymer material, should not be neglected. A recent simulation study suggests that the T_g for ultrathin films reflects a redistribution of mass in the film space rather than a simple competition between regions with different mobilities.³⁴ Indeed, it is not reasonable to consider that the ΔT_g behavior is exclusively an interfacial effect. As the glass transition is essentially a kinetic phenomenon, its mechanism has some complexity, which depends on the evolution of non-equilibrium states and cannot be characterized by a simple idealized treatment (for example, by a single-order parameter).³⁵

Another possible origin for the increase in T_g observed for the crosslinked shells of PVAc and polystyrene, as contrasted to spin-cast films, may be a crosslinking effect. Note that for non-crosslinked shells, no T_g deviation from the bulk was observed for polystyrene.¹⁴ In crosslinked polymers, structural relaxation is more difficult to occur than in non-crosslinked systems, and thus, unstable configurations (segment packing structure) tend to be retained even after annealing at a temperature above T_g . Therefore, the configuration in a crosslinked filled shell may be almost identical to that of the as-polymerized shell formed kinetically by random copolymerization with the crosslinking monomer. This configuration may not be thermodynamically stable in general and may differ from that of the bulk state. This tendency is clearly seen for crosslinked polystyrene shells with distinct differences in T_g and $\xi(T_g)$ from the bulk values.¹⁶ Accordingly, the results in Table 3 suggest that the as-polymerized configurations of crosslinked PMMA shells are relatively stable and closer to the bulk state. A PMMA shell prepared by a different method (adsorption method) showed a distinct depression of T_g from the bulk value, suggesting that the T_g deviation depends on the mechanism of shell formation.¹⁷ However, we should note that the above PMMA shell is considerably thin (8 nm). A reduction in $\xi(T_g)$ is found for PVAc and polystyrene shells, whereas little deviation is observed for PMMA shells. This result may be reasonably understood by assuming that the variation of $\xi(T_g)$ reflects the change in the distribution of segmental relaxation times caused by the difference in the configuration from an equilibrium state. We should emphasize here that the hypothesis of a crosslinking effect on the configuration is merely a rationalization of the observed behaviors. Further investigations should be performed to elucidate the configurational structure of the nanosized shells.

CONCLUSION

We have shown that rod-like core/shell capsules of PVAc/ CaCO_3 can be prepared by suspension copolymerization with a crosslinking reagent, triallyl isocyanurate. The thickness of the shell was 12–19 nm and was independent of the amount of fed monomer. Thicker shells could not be obtained by the present method; increasing the amount of

Table 3 Differences between the shell and bulk glass transition parameters

Polymer shell	ΔT_g^a	$\Delta \xi(T_g)^a$
Crosslinked PVAc	Positive (< 8 K)	Negative
Crosslinked PS	Positive (< 17 K)	Negative
Crosslinked PMMA	0 ~ negative	0 ~ negative

Abbreviations: PMMA, poly(methyl methacrylate); PS, polystyrene; PVAc, poly(vinyl acetate);

T_g , glass transition temperature; $\xi(T_g)$, dynamic length scale at T_g .

^a $\Delta T_g = T_g^{\text{shell}} - T_g^{\text{bulk}}$, $\Delta \xi(T_g) = \xi(T_g)^{\text{shell}} - \xi(T_g)^{\text{bulk}}$.

monomer fed in the reaction only increased the number of spherical particles without thickening the shell. Hollow capsules were not obtained by an acid treatment likely owing to the instability of the PVAc shell. The PVAc thin shells have higher T_g s and lower characteristic length scales at T_g than the bulk values. These results suggest the existence of unstable configurational effects, although the surface/interface effects should also be considered as well. The configurational effects may be more significant for crosslinked systems where the unstable structures (as-polymerized state) tend to be retained. It is intriguing that the deviations between the T_g and $\xi(T_g)$ of the shells and the bulk samples are different for the PVAc and polystyrene systems and the PMMA system, likely reflecting the different strengths of the individual factors that control the dynamics in nanosized polymers.

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