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REVIEW ARTICLE

Preparation of polymer nanoparticles, and the effect of nanoconfinement on glass transition, structural relaxation and crystallization

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In this review the preparation methods of polymer nanoparticles from chemical microemulsion polymerization to physical methods such as spray-drying, freeze-drying, freeze-extracting, fast evaporation and spreading evaporation have been summarized. The influence of nanoconfinement on glass transition temperature (T_g) variation from significant or slight decrease, no evident T_g deviation, to even T_g increase, as well as possible explanations of T_g deviations were discussed. The influences of nanoconfinement or entanglement on the other properties such as structural relaxation, crystallization in polymer nanoparticle samples were also reviewed in this article.

Keywords confinement, nanoparticles, glass transition, structural relaxation, crystallization

1 Introduction

The properties of polymer chains in nanoconfined states deviating from that of bulk have attracted extensive attentions, because such systems influence the conformation and interpenetration of molecular chains and showed special behavior in both thermodynamic and dynamic properties. Understanding the properties of polymers confined to nanoscale are of great value for emerging applications from polymer nanocomposites for structural applications to nanostructured films for plastic solar cells, and to polymeric membranes for energy efficient separations and drug delivery via polymeric carriers [1–5]. From the theoretical point of view, some fundamental questions of polymer science, such as crystallization, glass transition and structural relaxation behavior, can be addressed by comparing the properties of nanoconfined polymers with those of bulk polymers.

Most studies of the properties of nanoconfined systems have focused on the behaviors of polymer thin films, including singly and doubly supported films and freestanding films, which can be defined as the one-dimensional confinement. However, only a handful of studies have addressed the investigations about polymer confined in nanopores of controlled pore [6–8], polymer nanocomposites [9–11], and polymer nanoparticles which can be defined as the three-dimensional confinement [12,13]. The glass transition of these systems has received particular attention but it has not yet been fully understood. Keddie et al. discovered that polystyrene (PS) films supported on silica wafer exhibited a dramatic reduction in T_g with decreasing thickness [14], whereas poly (methyl methacrylate) (PMMA) films exhibited a thickness-dependent glass transition temperature (T_g) [15], which has led to a huge scientific and technological interest in understanding the phenomenon. T_gs of nano-films as measured by flurescence spectroscopy, X-ray reflectivity, dielectric relaxation spectroscopy, Brillouin scattering, and viscosity measurements, as well as computational simulations, all depended on the film thickness and the molecular weight of the polymer [16–20], and the glass formers confined in nanopores showed a reduced T_g [21,22]. Polymeric nanoparticles also exhibited a deviation of glass transition from the bulk with different preparation methods and polymer structures. In addition to exploring the glass transition of the nanoconfined systems, other important properties, such as physical aging (structural relaxation) and crystallization have also been studied. For example, Huang et al. [23,24] prepared several polymer samples such as polycarbonate (PC), poly (phenolphthalein ether sulfone) (PES-C) and polystyrene (PS) by fast-evaporation method from dilute solution, and the samples showed much lower structural relaxation behavior without exception. Li et al. [25] found that the atactic PMMA prepared in microemulsions showed higher structural relaxation than those of the bulk sample of the same tacticity and the same molecular weight, and the additional enthalpy relaxation moved to higher temperatures when the annealing time got longer. Sasaki et al. [26] observed two-step cold crstallization of poly (L-lactide) (PLLA) with a lower exotherm appearing at a temperature as low as 50 k lower than that having happened for a reference bulk sample, and with a higher and broad exotherm at high temperatures.

In this overview, the preparation methods of nanoparticle polymer samples by both physical and chemical methods are summarized, and a brief review of the glass transition of the confined systems, as well as their structural relaxation and crystallization, will be discussed compared to those of nanoconfined films. Some factors including entanglement,

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interfacial interactions, conformation, and sample preparation, which have caused different properties from the bulk, are also explored respectively.

2 Preparation methods of polymer nanoparticle samples

Polymer nanoparticles can be obtained by either chemical or physical route. For instance, the nano-size particles can be chemical synthesized by free-radical polymerization in microemulsions. In addition, several physical methods have been employed to obtain polymer nanoparticles, all relying on the isolation of the macromolecular coils from dilute solutions. The solutions are well below a critical overlap concentration, C^*, where physical contact among macromolecules starts as proposed by de Gennes [27]; or they may be even lower than a dynamic contact concentration, C_s, at which the coils have already contacted due to molecular motion as proposed by Qian et al. [28], who argued that only below C_s, coils are well-separated in the solution. C_s is usually 1–2 orders of magnitude lower than C^*.

2.1 Microemulsion polymerization

Polymerization reactions, when performed in microemulsion, can result in latex nanoparticles with a well-defined size and surface structure. The three-component microemulsion system usually includes oil, water phase and surfactant, and the concentration of surfactant that forms the interphase between the oil and water phases determines the dimension of the nanoparticles within a certain range. The polymer nanoparticles formed in microemulsions are PS [29–34] and PMMA [25,34,35] latex particles which exhibit particular characteristics. Recently, Zhang et al. [36,37] have obtained the soft (aqueous suspended PS particles) and hard (PS/silica core-shell particles) confined nanospheres and analyzed the glass transition and structure relaxation behaviors.

2.2 Spray-drying

Spraying method has been applied to a variety of different polymers, which relies on the evaporation of the solvent from sufficiently small droplets containing single or few polymer molecules by nebulization. It enables single-chain nanoglobules with clear outlines to be prepared. Xue et al. [38–40] elaborated on the spray-dryer and the auxiliary in detail and got PAL nano-sized particles verified by transmission electron microscope (TEM) and scanning electron microscope (SEM). Festag et al. [41] obtained single- and few-chain PS particles by electro-spray, and found the size of the particles can be controlled according to different spray conditions, the concentration of solution.

2.3 Freeze-drying

Freeze-drying method is used frequently in obtaining single-chain particles samples from dilute polymer solutions. The freeze-dried sample is usually prepared by dissolving the desired amount of the bulk sample and dispersing evenly in a mass of pure solvent, then the dilute polymer solution is injected into liquid nitrogen for shock-cooling, and then the frozen solution is sublimated under high vacuum so that the isolated nanoparticles could be obtained.

For instance, two distinct single-chain particles of poly (N-isopropylacrylamide) (PNIPAM), compact-globule state and loose-coil state, were prepared below and above the lower critical solution temperature in extreme dilute aqueous solution by the freeze-drying method [42]. Liu et al. [43] and Chang et al. [44] assumed that the extent of chain entanglement remains unchanged during the rapid freezing so that, after the removal of the frozen solvent by sublimation, the material should retain a memory of the chain interpenetration that has existed in the original solution.

2.4 Freeze-extracting

This method is similar with the freeze-drying way, but the difference is that the frozen solution is extracted with another cold solvent reiteratively after frozen by liquid nitrogen. The recovered sample does exist in the form of the confined molecular chains which may preserve the state in dilute solution to some extent [45–49].

2.5 Fast evaporation

Huang et. al reported the preparation of several kind of polymer nanoparticle samples by fast evaporation method [23,24]. In this method the selection of polymer solvent is very critical, it should have much lower boiling point than the heating liquid bath, and the density of solvent should be higher than that of bath liquid. Considering the above information, chloroform or dichloromethane are ideal solvents for this method. When dilute polymer solution was dripped into the boiling water which was kept in a constant temperature regulator, it will sink in the boiling water and evenly heated, and the solvent will evaporate in a split of second, leaving the fluffy sample on the water surface.

2.6 Spreading-evaporation

Kumaki [50–52] reported the preparation of polymer nanoparticles by spreading dilute polymer solution on water surface. In this method, the density of solvent should be lower than water, so the polymer solution will float on the water surface and spread out and form into monolayer of polymer nanoparticles after evaporation of the solvent.

3 Glass transitions of polymer nanoparticles

Although the glass transition of amorphous polymers has intrigued extensively scientific attention and technological interest, understanding the nature of glass transition still remains one of the most intriguing puzzles in condensed matter physics at present [53]. For a better understanding of the complicated problem, the glass transition of polymers confined to nanoscale has been studied by a lot of researchers, and T_g-deviation of the system, the case of three-dimensional confinement, has been reported for different polymers previously.

3.1 Deviation of glass transition temperature

3.1.1 T_g reduction

The depression of the T_g has been observed for nano-latex PS spheres, the freeze-dried samples and precipitated samples from dilute solution. Gaur and Wunderlich [54] investigated DSC curve of the nano-size PS spheres and found a decrease in the onset temperature of the glass transition, and the shift of the onset temperature of glass transition became less with the increasing size of the spheres. Ding and Xue et al. [55,56] reported much larger reduction (40–64 K) in T_g of freeze-dried and spray-dried PS, and T_g gradually approached the bulk value on repeated heating scans, whereas depression (2–15 K) of T_g were also reported for various PS freeze-dried from dilute benzene solutions. For instance, Simon et al. [57,58] investigated the calorimetric glass transition of linear and cyclic PS. For linear PS, the depression in T_g was found to be 2.2 K for the lowest molecular weight, 5.2 K for moderate molecular weight, and 3.0 K for the ultrahigh molecular weight; but for cyclic PS, T_g reduced 7–14 K and did not depend on the molecular weight, which indicated that the entanglement concentration was not responsible for the reduction in T_g. Huang et al. [23,24] obtained the single chain particles of polycarbonate (PC), polystyrene (PS), and phenolphthalein poly (ether sulfone) (PES-C) by rapid vaporization of solvent from dilute polymer solutions, and found that no reduction of T_g occurred for polymer concentrations greater than a critical value and T_g depression increased as the concentration decreased; they explained the T_g reduction resulted from the polymer chain disentanglement, which promoted the mobility of the chain segments. Rong et al. [59] also found that below a critical concentration the T_g of the samples decreases linearly with the decreasing logarithmic concentration of solutions. Recently, Zhang et al. [36] synthesized smoothly soft and hard confined PS nanoparticles with monodisperse dimensions, and found the size-dependent effects on T_g of soft nanoparticles, but no size dependence on T_g of hard nanoparticles was observed; these results were explained in the effect originating at the polymer free surface.

3.1.2 T_g increase

It should be noted that a depression in the T_g for nanosize polymers is not a universal observation. The enhanced T_g from the bulk value has also been reported. For example, Mi et al. [38–40] prepared nano-sized single chain particles of polyacrylamide by spray-drying and found that the T_g increased in comparison with that of normal bulk polymer; they suggested the increase of T_g in terms of cohesional entanglements formation during the preparation. In addition, Pilcher et al. [35] and Li et al. [25] investigated the glass transition behavior of poly (methyl methacrylate) polymerized in microemulsions, and discovered higher T_g than those of the bulk sample.

3.1.3 No evident T_g deviation

Many studies on spheres from microemulsion have indicated that T_g is almost the same as the bulk value. Ediger and coworkers [32] investigated the glass transition of PS microspheres, and reported that for spheres ranging from 42 to 548 nm, there was no significant change in the T_g although the value of the step change in the heat capacity at T_g decreased with the decreasing particle size. PS microspheres prepared by Ming et al. [31] displayed two exotherms near 107°C and 157°C during the first scan, but in the subsequent scan, both exotherms disappeared and only one glass transition similar to ordinary PS was shown. These results are similar with those of Qian et al. [30].

To be precise, the effect of nanoconfinement on the change of glass transition temperature in polymer systems reported in literatures is controversial. Significant decreases, no obvious deviations, and even increases of glass transition temperature have been reported in different research groups. The change of glass transition temperature seems also dependent on different preparation methods.

3.2 Some possible explanations of T_g deviations

3.2.1 Entanglements

Entanglements developed from the interpenetration of random-coil chains are important in determining rheological, dynamic, and fracture properties. It is well known that the topological entanglement of interlocked chain loops is the characteristic of bulk polymers. The existence of entanglements is usually considered to prohibit the mobility of the segments in the polymer. Thus, the decrease of entanglement promotes the mobility of the segments, and the glass transition

temperature consequently decreases. When polymeric molecules are in the isolated molecular state, such interlocking of the chain loops should not be significant. T_g-reduction, which depends on the concentration of the solution [23,24,59] and molecular weights [57], seems to have demonstrated the influence of topological entanglement, the reduction of T_g due to the decreased topological entanglement concentration. But T_g-increase is not well understood. Xue et al. explained the increase of T_g of PAL by the cohesional entanglement, which was supposed by Qian et al. [60], is the local nematic interaction between chain segments due to van der Waals force, hydrogen bonding, or hydrophobic ordering, etc., so although the topological entanglements decrease, the cohesional entanglements increase, especially after annealing, which has caused the increase of T_g. For T_g-depression of samples freeze-dried dilute solution, they held the existence of the less cohesional and topological entanglements accountable [61]. If the explanation is reasonable, it seems that T_g-deviation is dependent on the cohesional entanglement formation when the topological entanglements are lowered. In other words, if the intrachain cohesional entanglement density in single-chain particles is higher than the average interchain entanglement density in bulk polymer, the T_g of the single-chain sample may get higher.

Both theoretical [27] and computer simulation [62] investigations predict that polymers are highly segregated in two dimensions. An ideal random walk will occupy all sites within its perimeter in two dimensions, and the square of the end-to-end distance R_{EE} is equal to the area of the molecule ($R_{EE}^2 = N_a^2$, a is the length of a segment). Consequently, there is only negligible interpenetration for ideal random walks in two dimensions. If Φ is defined as the concentration of a particular chain within its envelope volume as the internal concentration, the larger Φ gets the lower possible paths for other chains through the envelope volume of a particular chain, for random walks $\Phi = N^{-1/2}$ and $\Phi = 1$ in three and two dimensions, respectively. For the confined polymer film, it is a quasi-two-dimensional state in between, so the extent of interpenetration is reduced compared with the bulk. Some experiments have demonstrated less entanglement of thin films, but there is still no complete consensus whether or not such low entanglement concentrations are responsible for the depression of the glass temperature in thin polymer films [63–66].

3.2.2 Free surface

According to the free-surface theory, the free surface of a bulk sample is really quite negligible, but for the nanostructures, the surface is very important due to the high surface to volume ratio. The reduction in T_g values is the result of the existence of a "liquidlike" layer near the free surface of the thin film. The layer model portrays the films as consisting of a highly mobile surface layer on top of a less mobile, largely bulklike inner layer. Keddie et al. [14] hypothesized that the surface mobile layer exists below the bulk T_g ($T_{g,bulk}$), and when the temperature T is increased toward $T_{g,bulk}$, its thickness diverges critically, following $\sim(1 - T / T_{g,bulk})^{-\nu}$, where ν is a constant between 0.56 and 1. As a result, thinner films can be filled with the surface mobile layer and get melt at a lower temperature. The T_g of thin film is described by a single empirical relation of the form:

$$T_g(h) = T_{g,bulk}\left[1 - \left(\frac{\alpha}{h}\right)^{\delta}\right]$$

Where $T_g(h)$ is the glass transition temperature for a film of thickness, h; α is a characteristic length [67]. The nanospheres can be similarly considered the core/shell model: the core of the sphere is bulklike and the core is surrounded by a mobile layer, which has a substantially lower T_g than the bulk.

Chang et al. [36] used the free surface theory to explain the T_g-reduction of the soft confined nanoparticles, and found striking similarity of size-dependent effects on the T_g of polymer nanoparticles and freestanding films [68], but the hard confined nanoparticles exhibit no change of T_g due to the confinement of the free surface of particles, which seems to be consistent with the finding of Rittigstein et al. [69]: Doubly silica-supported PMMA films exhibit a greater T_g increase with confinement than singly supported films.

3.2.3 Thermodynamic transition

Lu et al. [40] have provided a tentative explanation about the glass transition from a basic state equation:

$$\Delta G = \Delta H - T_g \times \Delta S$$

When there exists stronger molecular interaction between chain segments, the transition enthalpy increases and the transition entropy decreases, so T_g for the disentangled polymer should increase. However, the hydrophobic polymer is normally short of the strong interaction between chain segments. The conformational entropy difference between the disentangled polymer and an entangled system should follow the equation:

$$\Delta S_b < \Delta S_d$$

The subscript "b" means "bulk" and the subscript "d" means "disentangled." Supposing even the similar transition enthalpy (ΔH), a decreased T_g can be obtained for the disentangled hydrophobic polymer.

3.2.4 Change in specific structure or chain conformation

The polymer chains in the single chain system may adopt a highly compact conformation due to the spatial limitation, which occupies only a small percentage of random-coil volume as well as more equilibrium than de Gennes [27] pointed out. Yin et al. observed the T_g of single-chain sample of PNIPAM in compact-globule state was near to that of the bulk polymer, whereas the T_g of single-chain sample of PNIPAM in loose-coil state was approximately 6 K lower than that of the bulk polymer [42]. Xue et al. found that the interchain distance in the freeze-dried PS from a 0.1 wt % solution in benzene was larger, whereas interchain proximity in PS recovered from 20 wt % solution in benzene was of the same level as that in PS-cast film, which were supposed to be fully entangled, and the segments were compacted closely. Ming et al. [31] prepared the PS microspheres by microemulsion polymerization, which were analyzed to adopt a special conformation and form localized ordered regions in microspheres possibly due to the phenyl ring effect as Napper argued [70].

3.2.5 Reduction of density

The depression of T_g in thin films was blamed for the decreasing density by Reiter [71]. However, Wallace et al. [72] found the density was close to that of the bulk and was not a function of thickness. They ruled out the possibility that mass density is the underlying variable controlling polymer thin film behavior.

As for the single- or pauci-chain nanoparticle, the main interpenetrating and entanglement of segments are intramacromolecular, and a substantial fraction of the nearest-neighbor segments in the space are necessarily segments of the same chain. But in the case of the bulk, there exists mainly interchain interpenetrating and entanglements. So polymer nanoparticle has a loose structure and lower density in contrast to the bulk. Pouyet et al. [73] investigated the density difference between the ordinary PS and freeze-dried PS. Wu [74] has determined that the density of micro-PS is 0.92 g $\cdot$cm^{-3} by laser light scattering, which is much smaller than 1.05 g$\cdot$cm^{-3} of ordinary PS. Kumaki [52] found a significantly lower density of single-chain particles by accumulation on a substrate spread on water than multichain PS.

Although many explanations have been proposed, the cause of T_g-deviation from the bulk value upon rapid drying techniques from dilute solution has not been understood. On one hand, the deviations of T_g from the bulk obtained by various researchers are quite different. On the other hand, the experiments themselves are dubious. For instance, the freeze-drying process should consist of rapid solidification such that entanglement density and chain interpenetration are similar to the dilute solution state, and the process should result in complete solvent sublimation. But the former is difficult to accomplish in reality [75], and complete solvent removal is also difficult to achieve [76] as Simon proposed.

4 Structural relaxation behaviors of polymer nanoparticles

Structural relaxation is the spontaneous process of amorphous materials in the glassy state toward the thermodynamic equilibrium state, which involves the rearrangement of the microstructure in polymer. It can be detected through the time evolution of thermodynamic properties such as specific volume or enthalpy, as well as mechanical or dielectric properties. Few studies have characterized the structural relaxation of nanoconfined polymer glasses.

Huang et al. [23,24] found that the enthalpic peak of the single-chain sample by a fast evaporation method was lower than that of the bulk, which corresponded to the lower T_g; the peak was lower and broader, and the relaxed enthalpy was much lower when compared with that of bulk sample. They explained that the sample adopted a highly compact conformation and was in a greater equilibrium. Xue and coworkers [77,78] investigated the structural relaxation behaviors of partially disentangled poly (vinyl chloride) (PVC) samples prepared by freeze-extracting, and found that the endothermic enthalpy increased rapidly with decreasing solution concentration, and that the relaxation rate of the sample prepared from very dilute solution was higher than that prepared from more concentrated solution in tetrahydrofuran (THF). They ascribed the distinctive feature to the effect of entanglement in the polymer, which was in good agreement with the modeling predictions of Hodge, Gomez Ribelles and Cowie [79–81]. However, the structural relaxation of PVC obtained from concentrated solution in dioctyl phthalate (DOP) could exhibit similar relaxation with that produced from dilute solution in THF. Later, they studied the PS sample from dilute solution in benzene by freeze-drying and the sample from concentrated solution in DOP by freeze-extracting, and found that if the intersegmental distance was controlled to be larger than 0.5 nm, the enthalpy relaxation time spectrum through the glass transition region became narrower, and the stretch exponent β for the TNM model was larger; whereas the PS sample was a cast film or powder prepared from a concentrated solution, and the chains were detected to be in close proximity, thus their β value became smaller [82]. Structural relaxation of PMMA nanoparticles formed in microemulsions was also analyzed. Li et al. [25] observed a higher structural relaxation than those of bulk, and additional enthalpy relaxation at higher temperatures if the

sample was annealed; it explained the result of self-aggregation of the PMMA chains. The enthalpy relaxation peak of single-chain PAL nanoglobules was found to be sharper and higher than that of the bulk, whereas the partially entangled PAL exhibited two enthalpy relaxation peaks, which was attributed to the effects of topological and cohesional entanglement [38]. Recently, structural relaxations of PS nanospheres under soft and hard confinement were measured by DSC, and it was found that aging time to reach equilibrium for both soft and hard confined nanoparticles were longer than the bulk value, and that the aging rates of soft confined spheres were higher than bulk PS with decreasing diameter; whereas the hard confined spheres exhibited reduced rates compared to the corresponding soft nanoparticles, in accordance with the fact that there exists an internal positive pressure within the hard confined nanospheres [37].

The process of structural relaxation of polymer thin films has been investigated previously. A reduction of aging rate has been reported in supported thin polymer films, such as PMMA [83] and poly (2-vinylpyridine) [69], compared to the corresponding bulk polymer due to the interfacial effects, and simulations also find that a strong interfacial effect between polymer film and substrate can lead to suppressed aging of thin film [84]. In the absence of interfacial effects, the aging rate of thin polymer films can be comparable to or exceed that of the bulk [83,85,86].

5 Crystallization behaviors of polymer nanoparticles

Crystallization behavior polymer chains in a confined state were studied previously, and rapid crystallization of various polymers such as isotactic polystyrene [45,87–91], isotactic and syndiotactic polypropylene (PP) [46,92,93], polycarbonate (PC) [47,94], poly (vinylidene fluoride) (PVDF) [95], poly (ethylene terephthalate) (PET) [48], PLLA [26] and PMMA [49] by freeze-drying or freeze-extracting solutions were observed.

Xue and coworkers [48,95] obtained high crystallinity samples of PVDF and PET by freeze-extracting solutions, and found a concentration boundary in dilute solutions for crystallizability, i.e., the crystallinity was low in the concentrated regimes and increased rapidly as the concentration got more dilute, while below the critical boundary, crystallinity decreased with the decreasing polymer concentration due to too great distances between molecular chains. However, interestingly, the crystallinity of iPS from large molecule solvent (octadecyl benzoate), was independent of the solution concentration and was much higher than that for iPS samples crystallized by solution crystallization in a small molecule solvent [91]. Partially disentangled poly (vinyl chloride) prepared by freeze-extracting dilute solution in THF and concentrated solution in DOP also showed less interpenetration and high ordered conformations [77]. Isotactic PP freeze-extracted from n-octane solutions with varying concentrations were characterized by differential scanning calorimetry, and it is found that the sample recovered from the very dilute solution exhibited the higher non-isothermal crystallization temperature, faster isothermal crystallization rate; there should exist a critical concentration corresponding with the critical overlap concentration resulting in an acceleration of melt crystallization for the recovered samples [46].

A considerable amount of crystalline phase was formed in isotactic polystyrene (i-PS) by freeze-drying, and the sample could further crystallize through annealing, resulting in a much higher crystallinity than annealing an ordinary i-PS. Thermal analysis revealed that the collective particles crystallize much faster than bulk polymer, which was attributed to much fewer interchain entanglements within and between particles [48,94]. The disentangled particles of syndiotactic poly(propylene) (s-PP) freeze-dried from toluene solutions of various concentrations also showed high crystallinity and rapid crystallization rates [92]. Moreover, rapid crystallization of PC was achieved by freeze-drying dilute benzene solution, and it showed that there is a concentration boundary in very dilute solution for crystallizability of PC: Near the boundary concentration, the solution has a lower chain entanglement level, and as a result, crystallizes more quickly and completely than more highly entangled PC; through annealing, its crystallinity could reach a maximum value of 79.6%, which is much higher than that of annealing ordinary or other solution-crystallized samples [47]. Sasaki et al. [26] investigated the cold crystallization of freeze-dried PLLA by DSC, and found the samples obtained from a dilute solution underwent a two step cold crystallization: a lower exothermal peak appearing at low temperature due to high mobile chains of less chain-interpenetration; a higher broad exothermal peak at high temperature due to highly interpenetrated chains with low mobilities.

Metastable isotactic PS, an intermediate state between usual amorphous phase and crystalline, was prepared by freeze-extracting concentrated solution in solvents of middle molecular size, and it can be easily transferred to a highly crystalline state upon heating, which was attributed to fewer interchain entanglements [45]. Samples of iPP with various conformational orders prepared by freeze-drying from very dilute solutions showed high conformational order, which increased with the decreasing concentration of solutions [93]. Isotactic PS chains prepared by freeze-drying from dilute solutions adopted a similar state like those by freeze-extracting method [77,90]. In addition, some ordered

structures have been found to exist in samples of PS by microemulsion polymerization and PMMA by freeze-extracting during the heating process [31,49].

Recently, Wang et al. [96] investigated the role of reduced entanglements in the isothermal crystallization behaviors of iPP melts at moderate supercooling under unconfined condition, and observed that the in situ formed iPP spherulites can translate and/or rotate during isothermal crystallization even when the spherulite sizes grow exceeding the film thickness, whereas no traces of spherulite translation and rotation are observed in its entangled counterpart. They attributed the discrepancy to reduced chain entanglements.

To sum up the above results, it seems that the chain entanglement is a major cause to the crystallization of polymer besides the stereotacticity of itself. Disentanglement prompts the formation of ordered structures. However, for thin films with less entanglement than bulk, their crystallization behavior is more complicated for interfacial effects, and different preferential orientations of polymer crystals in thin films have been widely observed in experiments. With the decrease of the film thickness, the transition from edge-on to flat-on crystals has been observed in experiments of PEO [97], PDHS [98], and linear low-density PE [99], which reflects the influence of confinement by film thickness on the formation of the critical nucleus. In addition, the transition from flat-on crystals to diffusion-limited aggregates has been observed with the decrease of the film thickness of PCL [100], which reflects a competition between growth sites for polymers provided through long-distance diffusion across a depletion zone ahead of the crystal.

6 Conclusions and future perspectives

Nanoconfined polymer chains, which mean that the polymer exists in nanoscale dimension, are of considerable scientific and technological interest. In this article, we have reviewed the preparation methods of nanoparticles through both physical and chemical routes, and discussed the glass transition behavior of the confined systems, as well as their structural relaxation and crystallization behaviors, compared to those of nanoconfined films. Some factors including entanglement, interfacial interactions, conformation, and sample preparation methods, which cause the different properties from the bulk, are also explored respectively. However, in this field the experimental investigations go far beyond the theoretical and computational simulation studies. Many fundamental questions concerning the origins of the dependence of glass transition on the nanoconfined polymer systems remain unsolved. It remains a challenge to establish a widely accepted systemic theory to illustrate the nature of glass transition phenomenon and the effect of nanoconfinement on its deviation.

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