

# Understanding the Effect of Chain Entanglement on the Glass Transition of a Hydrophilic Polymer

Xiaolin Lu,<sup>1</sup> Gi Xue,<sup>2</sup> Yongli Mi<sup>3</sup>

<sup>1</sup>Department of Chemistry, Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Education Ministry, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China

<sup>2</sup>Department of Polymer Science, Nanjing University, Nanjing, 210093, People's Republic of China

<sup>3</sup>Department of Chemical and Biomolecular Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received 15 March 2010; accepted 1 June 2010

DOI 10.1002/app.32963

Published online 30 August 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** In this article, we report an interesting phenomenon of the glass transition temperature ( $T_g$ ) deviation of a hydrophilic polymer. Polyacrylamide (PAL) samples with different extents of chain entanglement were prepared by spray drying and solution casting. We found that the glass transition temperature increases as the extent of chain entanglement decreases upon the sub- $T_g$  annealing. The water content in the PAL matrix is found with no direct correlation to  $T_g$ . However, the observation of a faster diffusion process of water in the disentangled PAL matrix offers an evidence of a faster relaxation process of disentangled PAL molecules. The  $T_g$  increase of the disentangled PAL samples is believed to be associated with the increased molecular

interaction during the chain relaxation process upon the sub- $T_g$  annealing. A macroscopic evidence is the fact that the density of the hot-laminated samples increases as the extent of chain entanglement decreases. A thermodynamic analysis suggests that enthalpy more than entropy favors an elevated  $T_g$  of a disentangled hydrophilic polymer upon the sub- $T_g$  annealing. We believe that this research provides new understanding of  $T_g$  of the hydrophilic polymers, which are being extensively used in bio-related studies. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2310–2317, 2011

**Key words:** glass transition; hydrophilic polymers; differential scanning calorimetry (DSC); annealing

## INTRODUCTION

In the nearest several decades, the study of the glass transition of single chain polymers was focused with providing a valuable way to understand the glass transition behavior.<sup>1–10</sup> The generally accepted characteristic for such interesting single chain systems is short of the chain entanglement. The chain entanglement intuitively reduces the degree of freedom of the bond rotation and negatively affects the chain relaxation process. The existence of the chain entanglement in the long chain polymers have been proved by several approaches.<sup>11–20</sup> The chain disentanglement has been recognized as the reason for the  $T_g$  reduction of the several single chain poly-

mer systems. Gaur and Wunderlich<sup>1</sup> investigated the differential scanning calorimetry (DSC) curve of the nano-size latex polystyrene spheres and found a decrease in the onset temperature of the glass transition, and the shift of the onset temperature of the glass transition became less as the size of the spheres increased. Xue and coworkers found a decreased  $T_g$  of the freeze-dried polystyrene sample prepared from diluted solutions in the DSC experiment compared with the bulk sample and an enhanced structural regularity was also suggested due to observation of the sharper IR bands.<sup>2–5</sup> The enhanced structural regularity was further verified by Sasaki et al.<sup>21,22</sup> Huang et al.<sup>6,7</sup> obtained the single chain particles of polycarbonate, polystyrene, and phenolphthalein poly(ether sulfone) by a fast evaporation method;  $T_g$ s of such samples decreased compared to the bulk polymers, and they suggested that the  $T_g$  reduction was resulted from the chain disentanglement, which promoted the mobility of the chain segments. Bu et al.<sup>8</sup> prepared the freeze-dried isotactic polystyrene and attributed the  $T_g$  reduction and the fast crystallization rate to the chain disentanglement. Yang and coworkers<sup>9</sup> prepared the single chain poly(*N*-isopropylacrylamide) particles in the loose coil and the compact globular states, respectively.  $T_g$  of the single chain sample in the compact globular state is near  $T_g$  of the bulk polymer, and  $T_g$

Correspondence to: X. Lu (kelxl@163.com); Y. Mi (keymix@ust.hk).

Contract grant sponsor: Zhejiang Sci-Tech University; contract grant number: 0913845-Y.

Contract grant sponsor: Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Education Ministry, Zhejiang Sci-Tech University; contract grant number: 2009QN07.

Contract grant sponsor: Ministry of Education of Zhejiang Province; contract grant number: Y200909780.

Contract grant sponsor: HK Research grant RGC 617607.

of the single chain sample in the loose coil state was 6 K lower than  $T_g$  of the bulk polymer; upon repeated scans in DSC, both  $T_g$ s approached to  $T_g$  of the bulk polymer.<sup>9</sup> A totally different debate from Simon and coworkers<sup>10,23</sup> recognized that not the disentanglement but the residual solvent as the reason for the  $T_g$  reduction because repeated scans or annealing in the previous reports can gradually lustrate the residue solvent inside the polymer matrices. Remarkably, all the  $T_g$ s of the hydrophobic polymer systems in the previous reports do not exceed  $T_g$ s of their bulk states. However, Mi et al.<sup>24,25</sup> found that the hydrophilic polyacrylamide (PAL) single chain particles prepared by spray drying showed an elevated  $T_g$  compared to its bulk state. It suggests that a reinvestigation and a better understanding of disentangled polymer systems are needed, at least for a polymer system with the strong molecular interaction. As is known, an amorphous polymer goes through a transformation from the liquid state to the frozen glassy state as the temperature descends across  $T_g$ . Although most of the chain rotation freedom is lost in this supercooled glass, a slow relaxation may still proceed, which fortunately can be accelerated by the sub- $T_g$  annealing. A hydrophilic polymer and a hydrophobic polymer should behave noticeably different because the molecular interaction could affect this process a lot. In this article, we report an interesting  $T_g$  increase phenomenon of a hydrophilic polymer system with different extents of chain entanglement prepared from the diluted to the concentrated solutions by spray drying. A generalized understanding of the effect of molecular interaction and relaxation on  $T_g$  is provided.

## EXPERIMENTAL

### Preparation of the bulk film and the spray-dried particles with less chain entanglement

PAL (MW =  $5\text{--}6 \times 10^6$ , Polysciences, Warrington, PA.) was dissolved into the deionized water with a concentration of 0.5 wt %. The solution was cast on a flat Teflon surface. After the water evaporation, the bulk film was obtained. The PAL-deionized water solutions with five concentrations of 0.01 wt %, 0.02 wt %, 0.05 wt %, 0.1 wt %, and 0.2 wt % were prepared for spray drying. A Mobile Minor Basic Model Niro spray-dryer (Niro, Gladsaxevej 305, DK-2860 Soeborg, Denmark) was applied for obtaining the fluffy PAL particles with less chain entanglement. The method was discussed in a previous report<sup>26</sup> and will be introduced in Section Preparation and morphology of spray-dried PAL particles. During the process, the sample temperature was kept around 100–103°C for dehumidity.

The spray-dried particles and the bulk film were then placed inside a vacuumized desiccator with phosphorus pentoxide for more than 7 days.

### Hot-laminating and density test

The spray-dried particles and the bulk film were hot-laminated by a laminating press (PHI-Tulip, DT5000 controller and programmer, City of Industry, CA) at 170°C under 8 ton between two plates with the area of  $30 \times 30 \text{ cm}^2$ . The sample weight is 10 mg and the area of the compressed samples is  $15 \times 15 \text{ mm}^2$ . All the samples were preheated for 10 min. The pressure was kept for 10 min and then released after the temperature was cooled down lower than 50°C. After hot-laminating, the fluffy particles were molded into a film shape. The hot-laminated PAL spray-dried and the bulk film samples were annealed in an oven (Sheldon MFG, Shel Sab 1410, Cornelius, OR) at 180°C for 2 h, 8 h, and 16 h, respectively.

A density column (Techne, DC series, Burlington, NJ) was applied to test densities of hot-laminated samples. The toluene and dibromoethane as nonsolvents for PAL were used to prepare the solution with the density gradient ranging from  $1.2 \text{ g/cm}^3$  to  $1.5 \text{ g/cm}^3$ . The standard silicon beads were used to calibrate the density column.

### $T_g$ measurement

The differential scanning calorimeter (Perkin–Elmer Differential scanning calorimeter, Pyris 1, Perkin–Elmer, Waltham, MA) was used to measure  $T_g$ s of the samples. Before the experiment, the calibration by using the standard indium and zinc samples and the adjustments of the curvature and the slope of the DSC curve were carried out.

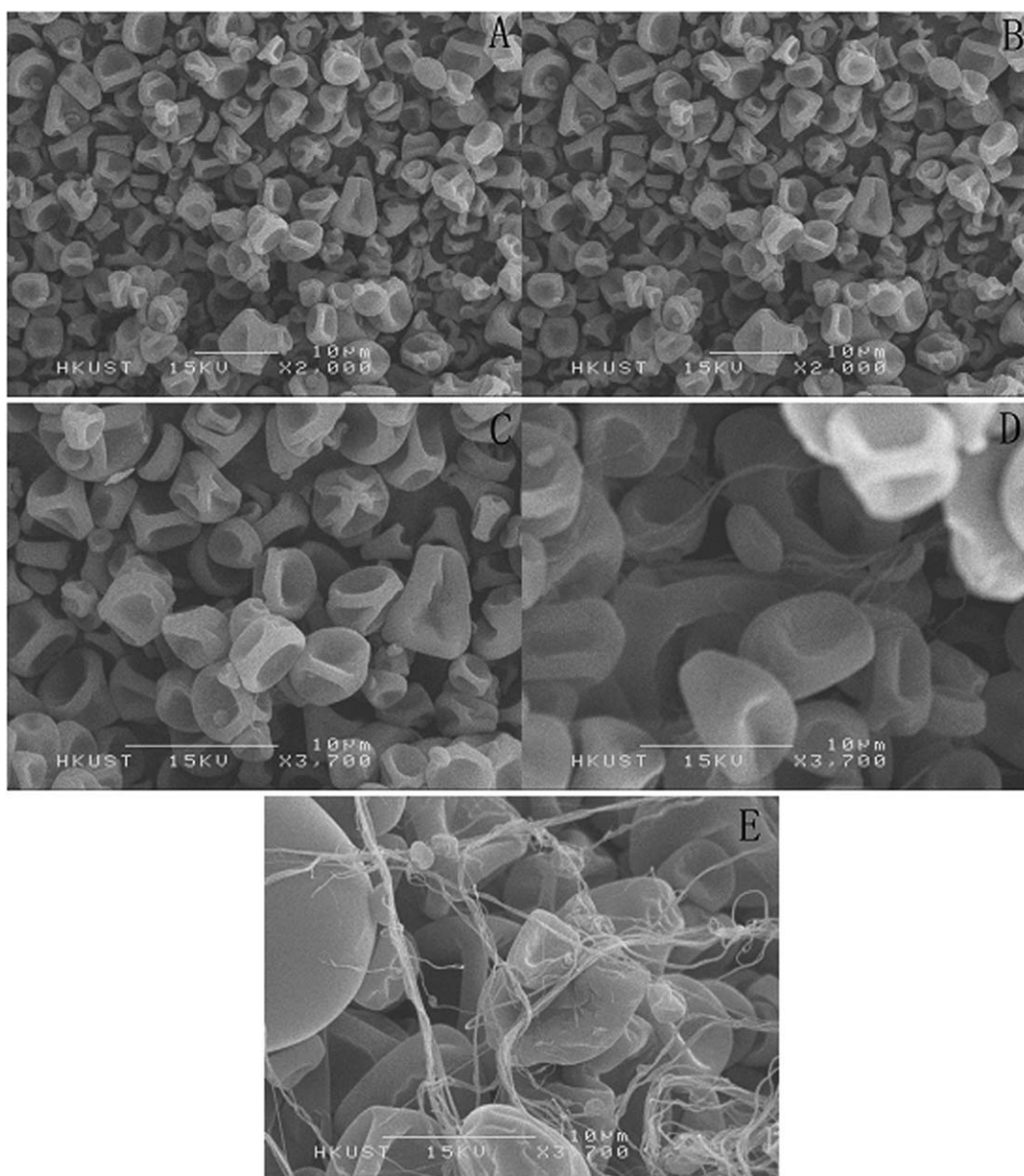
### SEM imaging

The scanning electron microscope (JEOL-6300F SEM, JSM 6300F, JEOL, Tokyo, Japan) was used to obtain the SEM images. A gold layer of 15 nm was sputtered (Denton Vacuum Desk II, INXS, Moorestown, NJ) on sample surfaces before the SEM imaging. The hot-laminated film samples were first immersed into the liquid nitrogen and then broken to acquire the cross section areas. Tilt was done for the film samples.

## RESULTS AND DISCUSSION

### Preparation and morphology of spray-dried PAL particles

The PAL-deionized water solutions with concentrations of 0.01 wt %, 0.02 wt %, 0.05 wt %, 0.1 wt %, and 0.2 wt % were used for preparing the PAL



**Figure 1** The SEM images of the spray dried PAL particles. A, B, C, D, and E were spray dried from the PAL deionized water solution of 0.01 wt %, 0.02 wt %, 0.05 wt %, 0.1 wt %, and 0.2 wt %, respectively.

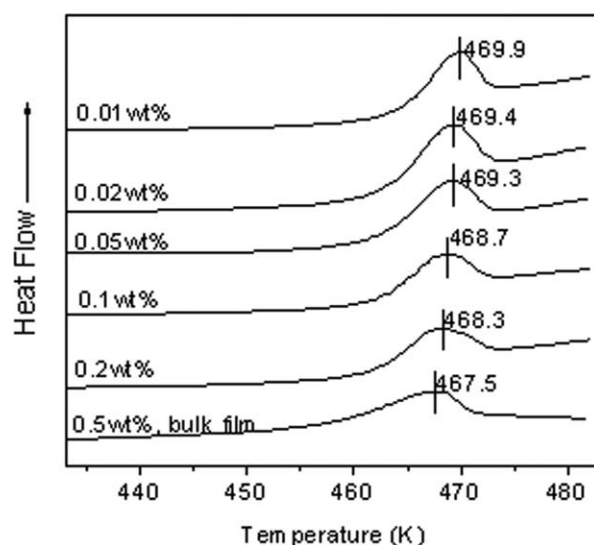
spray-dried particles. The main part of the spray dryer is the atomizer, which rotates at a high speed to convert the liquid into the small droplets. The extensive surface area and the introduction of the hot air provide a high efficiency for the solvent evaporation in a very short time. Supposing polymer chains in the diluted solution are in the isolated state, the fast evaporation of the solution droplets can produce the polymer single chain particles. Based on the concept of the overlap threshold in polymer good solvents,<sup>27</sup> the critical concentration for the molecular weight of  $5\text{--}6 \times 10^6$  is about 0.013 wt %, the disentangled PAL particles can be obtained from the 0.01 wt % solution. Another dynamic critical concentration was also suggested

by Qian and coworkers<sup>28</sup> considering the instantaneous overlap of polymer chains due to the macromolecular motion in the solution, which is 1–2 orders of magnitude lower than the critical concentration. The indication is that the spray-dried particles what we obtained from the 0.01 wt % solution may not be composed of only one polymer chain. However, according to the concentration sequence of 0.01 wt %, 0.02 wt %, 0.05 wt %, 0.1 wt %, and 0.2 wt % more and more overlapped PAL molecules in the solution can produce the spray-dried PAL particles with the increased extent of chain entanglement. The bulk film directly cast from the 0.5 wt % solution should have the highest extent of the chain entanglement.

Figure 1 shows a series of SEM images captured for the spray dried PAL particles. The different morphologies under SEM should be closely associated with the solvent evaporation process in the spray dryer referring to the droplet drying analysis.<sup>29</sup> When a droplet of the PAL solution was sprayed from the atomizer, the contact with the ambient hot air drove the evaporation of the deionized water solvent in a very high speed. There existed a wide droplet size distribution when the solution is atomized. If the droplet size was in the nano-scale, the total droplet lifetime is only milliseconds. The rapid evaporation left the less entangled or disentangled PAL chains, which self-aggregated to form the fluffy particles. If the droplet size was in the micron-size, the total droplet lifetime is several 10 or 100 milliseconds. The larger internal size and the relatively slow evaporation speed presented a PAL skin in the peripheral area of the droplet at first. The further evaporation of the inside water left the empty space inside and the thin PAL skin could not support to keep the perfect spherical geometry. The micron-size particles collapsed. The particles from the nano-size to the micron-size were observed in Figure 1. As the solution concentration increased, more fibrils were observed. It is suggested that the fibrils may be formed as follows. The overlapped polymer chains in the concentrated solution could not be separated during atomization and the polymer solution became gel-like. Part of the solution was sprayed as threads instead of droplets. As a result, fibrils composed of bundles of PAL molecules were left after evaporation.

#### Glass transition temperature of spray-dried PAL and the bulk film samples

Figure 2 is the DSC curves of the spray-dried PAL particles and the bulk film. All the samples were first heated up to 210°C to remove the thermal history. Then the samples were annealed at 180°C for 2 h and then quenched to 70°C in the Perkin-Elmer DSC chamber. After that, the samples were heated from 70 to 210°C at a heating rate of 10°C/min. Due to the sub- $T_g$  annealing, an enthalpy relaxation peak appeared for each sample, which is an indication of the glass transition.<sup>30</sup> In the normal case, the enthalpy relaxation peak can show the combined effect of the chain relaxation and the thermal history. Because the thermal history has been removed by heating up all the samples to 210°C before the sub- $T_g$  annealing, here the curve shape indicated by the enthalpy relaxation peak should be solely from the inherent glass transition of our samples. There are several methods to define the phenomenological  $T_g$ , such as the half heat capacity ( $C_p$ ) extrapolated point, the onset point, and the inflection point, etc.

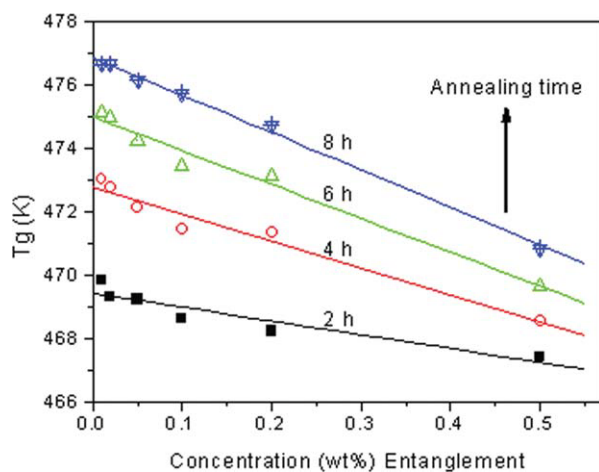


**Figure 2** DSC curves of spray-dried PAL particles after annealing at 180°C for 2 h.

In this study, because of the enthalpy relaxation peak, it is difficult to use the half  $C_p$  extrapolated point as the indication of  $T_g$ . When the inflection point across the enthalpy relaxation peak was defined as the indication of  $T_g$ , we found that  $T_g$  increased as the concentration decreased. We also found the same  $T_g$  deviation phenomenon if the onset point was taken as the indication of  $T_g$ . This suggests that the  $T_g$  deviation of our samples are not from the artificial effect but attributed to the intrinsic chain structural characteristic.

Besides, we thermally treated our samples over different annealing times, namely, 2 h, 4 h, 6 h, and 8 h, respectively. The collected  $T_g$ s in term of the concentration were plotted in Figure 3. Obviously,  $T_g$  increased as the concentration decreased for the same annealing time. The solid line was the linearly fitted curve of  $T_g$ s with respect to the concentration for each annealing time just to show the trend. It was also clear that a higher  $T_g$  was obtained provided that longer annealing time was given.

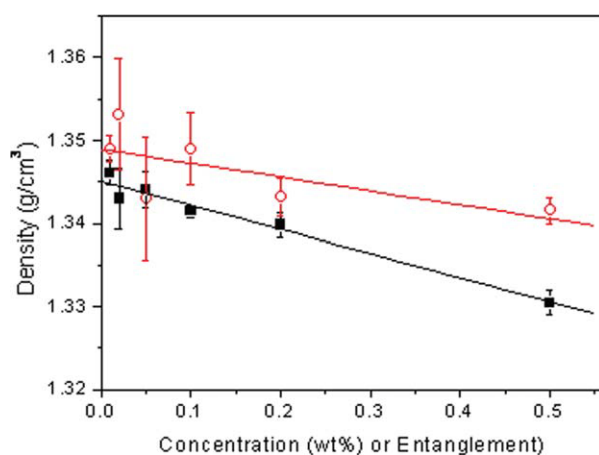
de Gennes<sup>27</sup> pointed out that the polymer chains in the single chain system may adopt a highly compact conformation as well as a more equilibrium state. Qian et al.<sup>31</sup> brought about the concept of the cohesive entanglement to be distinguished from the interlocked chain loops, termed as the topological entanglement. The cohesive entanglement is the local nematic interaction between chain segments, due to van der Waals force, hydrogen bonding, or hydrophobic ordering, etc. PAL molecules, with an amino group and a carbonyl group in the side chain, have a high potential to form the strong molecular interaction due to hydrogen bonds. Here, we buy this concept. Supposing less topological entanglement (disentangled chains) in the PAL structure, a faster



**Figure 3** The collected  $T_g$ s in terms of the initial solution concentration for different annealing times. The sub- $T_g$  annealing was run at 180°C for 2, 4, 6, and 8 h, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

relaxation process was expected during the sub- $T_g$  annealing and the relaxation was prone to offer more molecular interaction sites. It was anticipated that much stronger molecular interaction existed for disentangled chains and induced a higher  $T_g$ . For the same sample over longer sub- $T_g$  annealing time, the stronger molecular interaction can form, which caused a higher  $T_g$  than  $T_g$  with shorter annealing time.

The implication of more cohesive entanglement (or hydrogen bonds) is a high molecular packing density, the effect of which is hopefully observed in a macroscopic scale. Figure 4 shows the relationship



**Figure 4** The measured density in terms of the concentration for the hot-laminated samples. The solid squares represent the densities of the initially hot-laminated samples. The hollow circles represent the densities of the hot-laminated samples after annealing at 180°C for 2 h. The linearly fitted lines are used just to show the trend. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE I**  
Water Content of Spray-Dried Particles and the Bulk Film Annealed at 180 °C in the DSC Chamber

Solution concentration (wt %)	Initial water content (wt)	Water content after 2-hour annealing (wt)	Water content after 8-hour annealing (wt)
0.01	0.193	0.118	0.0735
0.02	0.144	0.0727	0.0295
0.05	0.171	0.117	0.0795
0.1	0.135	0.0798	0.0552
0.2	0.133	0.0915	0.0740
0.5	0.137	0.126	0.117

between the density and the concentration for the hot-laminated samples before and after annealing at 180°C for 2 h. Solids lines are the linearly fitted curves to show the trends for the solid squares and the hollow circles, respectively. As shown in Figure 4, the density increased for both the initially hot-laminated (the solid squares) and annealed (the hollow circles) samples as the concentration decreased. Although it was an indirect proof because all the samples have undergone a hot-laminating process, at least, we can conclude that the disentangled PAL sample has the very potential to be in a highly compact state upon the sub- $T_g$  annealing.

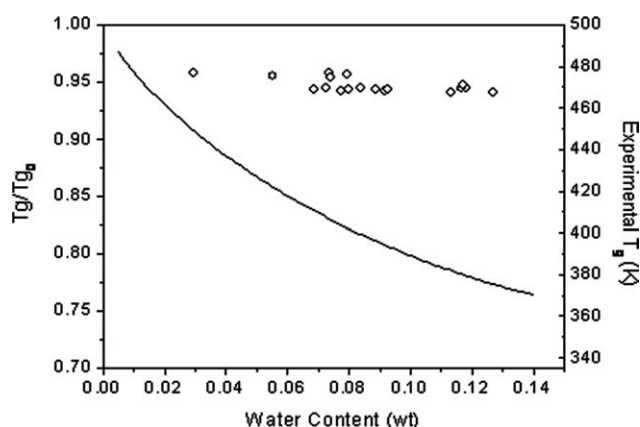
#### Effect of the water content

Because PAL is highly hydrophilic, the inclusion of water molecules in the structure could not be neglected. The water content was measured for the spray-dried and the hot-laminated film samples, shown in Tables I and II. The initial water content was taken as the water loss of the samples annealed at 180°C for 16 h in the vacuum oven. Chow<sup>32</sup> presented a model to correlate the  $T_g$  reduction with the dilution of small molecules, as express by the following eq.

$$\ln \frac{T_g}{T_{g^0}} = \beta[(1 - \theta) \ln(1 - \theta) + \theta \ln \theta] \quad (1)$$

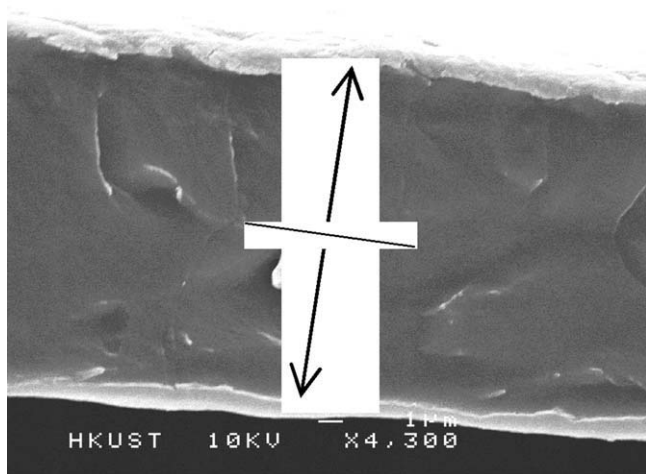
**TABLE II**  
Water Content of the Hot-Laminated Samples Annealed at 180°C for 2 Hours

Solution concentration (wt %) during preparation	Initial water content (wt)	Water loss (wt)	Water content (wt)
0.01	0.184	0.109	0.0839
0.02	0.133	0.0691	0.0686
0.05	0.157	0.0709	0.0927
0.1	0.126	0.0410	0.0886
0.2	0.115	0.0408	0.0774
0.5	0.129	0.0180	0.113



**Figure 5** The theoretical  $T_g/T_{g0}$  (solid line, left coordinate) and the experimental  $T_g$  (hollow dots, right coordinate) in terms of the water content.

$\beta$  is a parameter, which can be evaluated from the polymer molecular weight, the heat capacity difference between the liquid and glassy states;  $\theta$  is a parameter, which depends on the small molecule's concentration, the molecular weights of the polymer and small molecule. The model-predicted  $T_g$  and the experimental  $T_g$  in terms of the water content were plotted in Figure 5. Based on the model prediction, a water content of 10 wt % should produce a  $T_g$  decrease of several tens of Kelvin. Our experimental data did not show this large-scale  $T_g$  decrease. No obvious correlation was found between the water content and the  $T_g$  deviation of PAL samples. This also suggests that not water but the intrinsic chain structural characteristic should be responsible for the observed  $T_g$  deviation phenomenon, as indicated in Section Glass transition temperature of spray-dried PAL and the bulk film samples.



**Figure 6** The arrows show the water diffusion from the center (the transverse line) to the surface through a plate-shape sample. The SEM image is a hot-laminated bulk film sample.

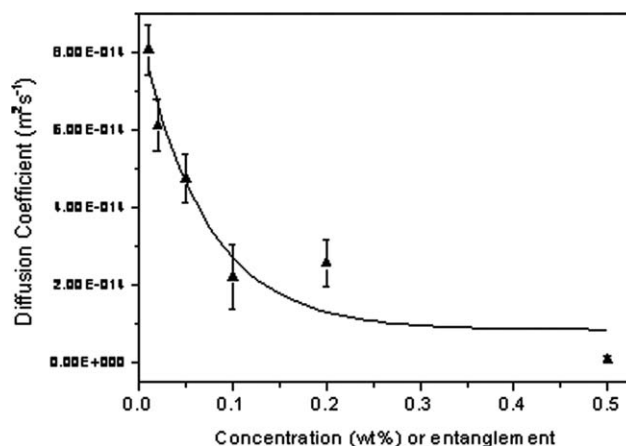
However, if the water loss of a hot-laminated film sample was considered, a simple model of one-dimensional diffusion could be applied as the following equation supposing the rate-limiting step is the diffusion of water through the PAL matrix to the surface,<sup>33,34</sup> where  $x_0$  is the initial water weight content;  $x_t$  is the water weight content after time  $t$ ;  $s$  is the half thickness of the plate;  $D$  is the constant diffusion coefficient. Figure 6 shows a SEM image of the cross section area of the bulk film indicating the water diffusion direction through the polymer matrix.

$$\left(\frac{x_0 - x_t}{x_0}\right)^2 = \frac{4}{\pi S^2}Dt \quad (2)$$

Based on the data in Table II of the hot-laminated samples with annealing at 180°C for 2 h, the calculated apparent diffusion coefficient ( $D$ ) in terms of the concentration for spray drying was plotted in Figure 7. The apparent diffusion coefficient decreased dramatically in the low concentration area and leveled off in the high concentration area. A higher diffusion coefficient is normally favored by higher chain mobility, which should be characteristic of the disentangled chains. This is also in agreement with the expected result in Section Glass transition temperature of spray-dried PAL and the bulk film samples that less chain entanglement corresponds to the faster relaxation process.

### Chain entanglement, relaxation, and $T_g$

The extent of the chain entanglement is believed to increase as the solution concentration for spray drying increases. The chain entanglement, functioning as physical crosslinked sites, should reduce the chain mobility by enlarging the cooperative length of the chain segment. A previous article has



**Figure 7** The apparent diffusion coefficient ( $D$ ) in terms of the solution concentration for spray drying. Solid line shows the change trend of the apparent  $D$ . Triangle dots are the experimental data with the error bar.

discussed this and an increased conformational entropy for the supercooled single chain globules was predicted; an elevated  $T_g$  is thus derived based on this.<sup>26</sup> The increased conformational entropy for the disentangled PAL samples is quite reasonable on account of its faster relaxation process. However, this increased conformational entropy is true only in the case that the chain segments are free or short of interaction. The sub- $T_g$  annealing, as well as the water diffusion, is a relaxation process toward forming the strong molecular interaction. The chain entanglement impedes or slows down this relaxation process by reducing the chain mobility. The chain rotation freedoms for a hydrophilic polymer, before and after the sub- $T_g$  relaxation, could be significantly different due to the confined effect from the molecular interaction. Analogously, it can not be expected that a loosely packed chain in a fluffy sample just spray dried has the same rotation freedom as a densely packing chain after annealing. The conformational entropy of a disentangled chain actually should reduce to a much lower value due to the confinement of the molecular interaction compared to an entangled chain provided the enough annealing is given.

If the glass transition is considered as a thermodynamic transition, the basic state equation is abided by:

$$\Delta G = \Delta H - T_g \cdot \Delta S \quad (3)$$

The formation of stronger molecular interaction definitely favors the increase of the transition enthalpy and the decrease of the transition entropy. An elevated  $T_g$  for a disentangled polymer is thus a collective result. One may consider, because a disentangled polymer upon annealing macroscopically holds a higher density than an entangled polymer does, the diminished free volume may also be the reason for the  $T_g$  increase. Actually, the diminished free volume can be taken as a consequence of forming the molecular interaction as well as the reduced conformational entropy. At least in the current stage, we prefer the enlarged transition enthalpy due to strong molecular interaction as the direct reason of the  $T_g$  increase.

A hydrophobic polymer is normally short of the strong interaction between chain segments. The chain mobility of a hydrophobic polymer can not be obviously reduced by a relaxation process as the sub- $T_g$  annealing. The chain entanglement could only have a negative effect on the conformational entropy, whether below  $T_g$  or above  $T_g$ . The impedence of the chain entanglement should have stronger effect on the liquid state (above  $T_g$ ) than on the glassy state (below  $T_g$ ). The conformational entropy

difference (above and below  $T_g$ ) between a disentangled polymer system and an entangled one should follow the inequation.

$$\Delta S_c^b < \Delta S_c^d \quad (4)$$

Superscript "b" means "bulk" and Superscript "d" means "disentangled." Even supposing the similar transition enthalpy ( $\Delta H$ ), a decreased  $T_g$  can be obtained for the disentangled hydrophobic polymer. From above analysis, a tentative conclusion may be drawn that enthalpy over entropy may play a more important role for the hydrophilic polymer whereas entropy over enthalpy may play a more important role for the hydrophobic polymer on the  $T_g$  deviations.

## CONCLUSIONS

The PAL bulk film sample and the PAL samples with different extents of chain entanglement were prepared by direct casting and spray drying, respectively. Upon the sub- $T_g$  annealing, an increased  $T_g$  with a decreased solution concentration as well as a decreased extent of the chain entanglement was observed in the DSC experiment. A highly molecular packing density in the disentangled PAL samples was suggested by observing an increased macroscopic density of the hot-laminated sample with the decreased extent of the chain entanglement. The water inclusion in the PAL samples was found with no correlation to the  $T_g$  deviation. The evaluation of the apparent diffusion coefficient of water indicated a faster relaxation process for the disentangled PAL samples. The relaxation with no impedence from chain entanglement was believed to be responsible for formation of stronger molecular interaction and the increased macroscopic density. A simple thermodynamic analysis suggests that enthalpy over entropy may play a more important role for the  $T_g$  deviation of the hydrophilic polymers and entropy over enthalpy may play a more important role for the  $T_g$  deviation of the hydrophobic polymers. We believe that this research provides a promising understanding of the glass transition for a hydrophilic polymer, which may raise much interest in the biophysics area because most of the previous reports about study of the glass transitions were involved in the hydrophobic polymers.

## References

1. Gaur, U.; Wunderlich, B. *Macromolecules* 1980, 13, 1618.
2. Ding, J.; Xue, G.; Dai, Q.; Cheng, R. *Polymer* 1993, 34, 3325.
3. Xue, G.; Wang, Y.; Gu, X.; Lu, Y. *Macromolecules* 1994, 27, 4016.
4. Xue, G.; Wang, Y.; Liu, S. *Macromolecules* 1995, 28, 4344.

5. Dai, Q.; Lu, Y.; Xue, G.; Liao, Y. T. *Polym Bull* 1995, 35, 209.
6. Huang, D.; Yang, Y.; Zhuang, G.; Li, B. *Macromolecules* 1999, 32, 6675.
7. Huang, D.; Yang, Y.; Zhuang, G.; Li, B. *Macromolecules* 2000, 33, 461.
8. Bu, H.; Gu, F.; Bao, L.; Chen, M. *Macromolecules* 1998, 31, 7108.
9. Yin, W.; Yang, H.; Cheng, R. *Eur Phys J E* 2005, 17, 1.
10. Bernazzani, P.; Simon, S. L.; Plazek, D. L.; Ngai, K. L. *Eur Phys J E* 2002, 8, 201.
11. Fujita, H.; Ninomiya, K. *J Polym Sci* 1957, 24, 233.
12. Ninomiya, K.; Fujita, H. *J Colloid Sci* 1957, 12, 204.
13. Fox, T. G.; Allen, V. R. *J Chem Phys* 1964, 41, 344.
14. Fox, T. G.; Loshaek, S. *J Appl Phys* 1955, 26, 1080.
15. Longworth, R.; Morawetz, H. *J Polym Sci* 1958, 29, 307.
16. Markovitz, H.; Fox, T. G.; Ferry, J. D. *J Phys Chem* 1962, 66, 1567.
17. McCall, D. W.; Douglass, D. C.; Anderson, E. W. *J Polym Sci* 1962, 59, 301.
18. Powles, J. G.; Hartland, A. *Nature* 1960, 186, 26.
19. Powles, J. G. *Polymer* 1960, 1, 219.
20. Slichter, W. P.; Davis, D. D. *J Appl Phys* 1964, 35, 3103.
21. Sasaki, T.; Tanaka, M.; Takahashi, T. *Polymer* 1997, 38, 4765.
22. Sasaki, T.; Tanaka, M.; Takahashi, T. *Polymer* 1998, 39, 3853.
23. Zheng, W.; Simon, S. L. *Polymer* 2006, 47, 3520.
24. Mi, Y.; Xue, G.; Lu, X. *Macromolecules* 2003, 36, 7560.
25. Mi, Y.; Xue, G.; Wang, X. *Polymer* 2002, 43, 6701.
26. Mi, Y.; Wang, J.; Zhang, Y.; Chen, E.; Cheng, S. Z. D. *Polymer* 2001, 42, 4533.
27. de Gennes, P. G. *Scaling Concepts in Polymer Physics*. London: Cornell University Press, 1979.
28. Liu, M.; Cheng, R.; Qian, R. *J Polym Sci: Polym Phys Ed* 1995, 33, 1731.
29. Masters, K. *Spray Drying Handbook*, 4th ed. New York: Halsted Press, 1985.
30. Berens, A. R.; Hodge, I. M. *Macromolecules* 1982, 15, 756.
31. Qian, R.; Wu, L.; Shen, D.; Napper, D. H.; Mann, R. A.; Sangster, D. F. *Macromolecules* 1993, 26, 2950.
32. Chow, T. S. *Macromolecules* 1980, 13, 362.
33. Aldous, B. J.; Franks, F.; Greer, A. L. *J Mater Sci* 1997, 32, 301.
34. Crank, J. *The Mathematics of Diffusion*, 2nd ed. Oxford: Oxford University Press, 1975.