1702 *Macromolecules* **2010**, *43*, 1702–1705
DOI: 10.1021/ma100012c

Macromolecules
COMMUNICATION TO THE EDITOR

# Spectroscopic Evidence of Melting of Ordered Structures in the Aged Glassy Poly(L-lactide)

**Bing Na,* Ruihua Lv, Shufen Zou, Zhujun Li, and Nana Tian**

*Department of Materials Science and Engineering,
East China Institute of Technology, Fuzhou, 344000,
People's Republic of China*

**Qiang Fu***

*Department of Polymer Science & Materials, Sichuan University,
State Key Laboratory of Polymer Materials Engineering,
Chengdu, 610065, People's Republic of China*

*Received January 4, 2010
Revised Manuscript Received January 20, 2010*

**1. Introduction.** As a supercooled liquid, polymer glass is thermodynamically unstable, and during annealing below the glass transition temperature (i.e., physical aging) its internal structure undergoes a slow relaxation toward equilibrium.[1] This process is experimentally manifested by the decrease in the volume, enthalpy, and segmental mobility with aging time.[2−6] Moreover, dense chain packing, accompanied by conformation transformation to stable state, is expected in the aged polymer glasses because of the reduction of free volume.[7,8] In this connection, some authors have claimed that a short-range ordered structure could be formed, as a result of local molecular motions, during aging of a glassy polymer.[6,8−11] Furthermore, destroying (melting) these ordered domains upon heating seems to give a plausible explanation of the endothermic peak which appeared in the glass transition region.[8] To date, unfortunately, convincing evidence regarding the ordered structure and its correlation with enthalpy recovery in the aged polymer glasses is still absent.

In the past decades glassy poly(ethylene terephthalate) (PET) is usually chosen as a candidate to address the aforementioned issues.[5,6,8−10] On the other hand, poly(L-lactide) (PLLA), a biodegradable polyester, is also susceptible to physical aging below its glass transition temperature ($T_g \sim 60$ °C).[12−15] Similar to PET, it is speculated that local order is increased during aging process, which could be the origin of significant enthalpy recovery during glass transition as well as enhanced cold crystallization.[16,17]

In this Communication, in situ Fourier transform infrared spectroscopy (FTIR), sensitive to the local molecular environment, is adopted to monitor the structural changes with respect to glass transition, cold crystallization, and melting process during a heating run of aged glassy PLLA. It is indicated that a sharp decrease of absorbance is observed during both glass transition and melting process in the aged PLLA. This similarity strongly suggests the enthalpy recovery (i.e., endothermic peak) in the glass transition region is originated from the melting of short-range ordered structures in the aged glass.

**2. Experimental Section.** The PLLA, supplied by Natureworks, had a melt flow index of 15 g/10 min and a relative viscosity of 3.2. Amorphous films with thickness no more than 50 μm were melt-pressed in a hot press at 200 °C, followed by quenching into ice water after being held for 5 min at molten state. Note that the sample was sandwiched between two thin polyester films during film preparation, and the same processing conditions were used. Aging of as-prepared films for a desired period was conducted at 50 °C under a nitrogen atmosphere. Temperature-dependent FTIR measurements were carried out by a Thermo Nicolet FTIR spectrometer equipped with a hot stage. The thermal behaviors were registered using a NETZSCH DSC 204.

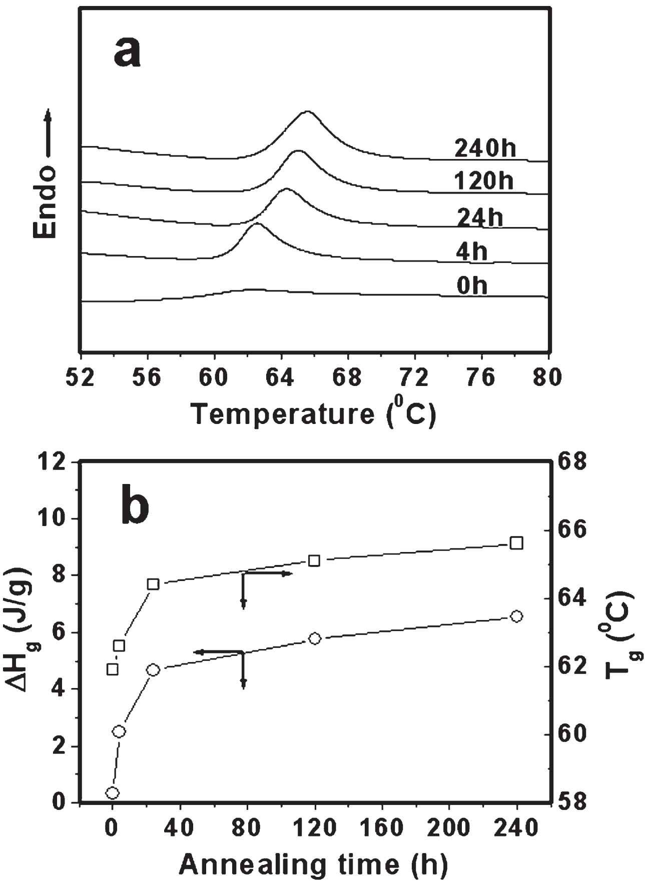

**Figure 1.** (a) DSC curves and (b) the corresponding $T_g$ and enthalpy of glassy PLLA aged for indicated periods.

**3. Results and Discussion.** Figure 1 shows DSC curves on heating at 5 °C/min of glassy PLLA aged for a desired period in the glass transition region. Similar to other aged polymer glasses,[1,5,8] an apparent endothermic peak is observed for the aged PLLA and the peak position and area are increased with aging time.[12−15] As regarding the enthalpy recovery during glass transition two opposite arguments have been proposed in the past. One is that the physical aging process is a free volume controlled event, and the aged sample has smaller free volume and enthalpy than the unaged one.[18] Thus, upon heating the steep increase of free volume as well as unfreezing of high-energy conformation around glass transition gives rise to endothermic peak as well as significant enthalpic effect. On the other hand, local order, accompanied by loss of free volume, seems to be created in the aged

---

*Corresponding authors: Fax 0086-794-8258320, e-mail bingnash@163.com, bna@ecit.edu.cn (B.N.); Fax 0086-28-85405402, e-mail qiangfu@scu.edu.cn (Q.F.).

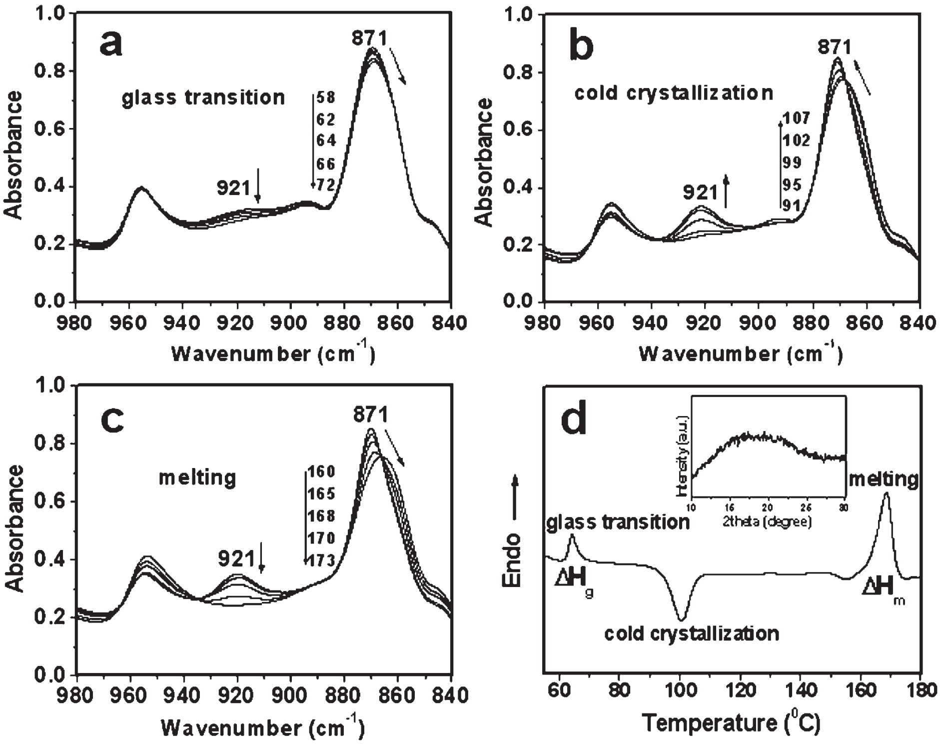

**Figure 2.** Temperature-dependent IR spectra related to the (a) glass transition, (b) cold crystallization, and (c) melting process during a heating run of glassy PLLA aged for 24 h. For comparison, the DSC curve reflecting aforementioned three transition processes is included in (d).

polymer glasses.[9,10] It is believed that the melting of short-range ordered structures is the origin of the endothermic peak appeared in the glass transition region, based on the fact that the energy consumed by the conformational change is far below the enthalpy determined from DSC.[8]

To clarify this critical issue, temperature-dependent FTIR measurements at a heating rate of 5 °C/min have been carried out, and a typical result obtained from the glassy PLLA aged for 24 h is presented in Figure 2. On heating from the glassy state three transition processes are observed in sequence, namely glass transition, cold crystallization, and melting, as demonstrated by the DSC curve shown in Figure 2d. The desired IR bands at 921 and 871 cm$^{-1}$, correspondingly, show apparent changes with respect to these three transition processes. In the glass transition region a decrease of the IR bands with increasing temperature is observed, which is similar to that occurring in the melting process but opposite to that appearing during cold crystallization.

Allowing that the cold crystallization and melting process are related to the formation and destruction of crystals, respectively, it means that during glass transition a certain structure could be destroyed even though long-range order is absent in the aged PLLA (evidenced by the diffuse X-ray diffraction profile in Figure 2d as inset). Recalling that the 921 cm$^{-1}$ band is assigned to the $10_3$ helix conformation[19,20] and the 871 cm$^{-1}$ band is sensitive to the intermolecular packing in the PLLA,[20] an absorbance decrease of 921 and 871 cm$^{-1}$ band corresponds to the melting of helical sequence (helix–coil transformation) and weakening of intermolecular packing on heating, respectively. In addition, as for the 871 cm$^{-1}$ band, the weakening of intermolecular packing can reduce the dipole–dipole interactions and thus give rise to its peak shift to low wavenumber,[19,20] as observed during glass transition and melting process. Note that the assignment of the 871 cm$^{-1}$ band to the intermolecular packing is further evidenced by its abrupt absorbance increase prior to dominant melting of crystals (see Figure 3), resulting from the transition from disordered α′-form crystal with loose intermolecular packing to the ordered α-form crystal with dense intermolecular packing[21] because of recrystallization or reorganization (manifested by a small exothermic peak in the DSC curve in Figure 2d).

For quantitative analysis of the change of helical sequence and intermolecular packing with temperature in the aged PLLA, the absorbance of 921 and 871 cm$^{-1}$ bands is deduced using local baseline, and the corresponding results are collected in Figure 3. For comparison, the results obtained from the unaged PLLA are also included. Interestingly, in the glass transition region a sharp decrease of absorbance is observed for both 921 and 871 cm$^{-1}$ bands in the aged PLLA, same to that related to the melting process. Rather, only a gradual decrease in the absorbance of 921 and 871 cm$^{-1}$ bands around glass transition is presented in the unaged counterpart. In this context, it is reasonable to claim that a short-range ordered structure with dense intermolecular packing, allowed by coil–helix conformation transformation, is indeed formed in the aged glassy PLLA. The melting of such local ordered structures around glass transition is the origin of the endothermic peak in the DSC curve,[8,16] which is essentially analogous to that observed for the crystals with long-range order. One may ague that (free) volume recovery during glass transition can also result in the decrease of absorbance especially for the 871 cm$^{-1}$ band which is sensitive to the intermolecular packing even though no local order exists in the aged PLLA. If so, it means that the intermolecular packing becomes dense as a whole during aging process while the free volume is reduced. As a matter of fact, it has been well demonstrated, by small-angle X-ray scattering measurements on the aged polystyrene, that the average and the distribution of free volume do not change in parallel and the short-range order of intermolecular packing is enhanced upon aging.[2,22] Thus, a sharp decrease of absorbance in the aged PLLA during glass transition is in nature resulted from the melting of local order rather than from the

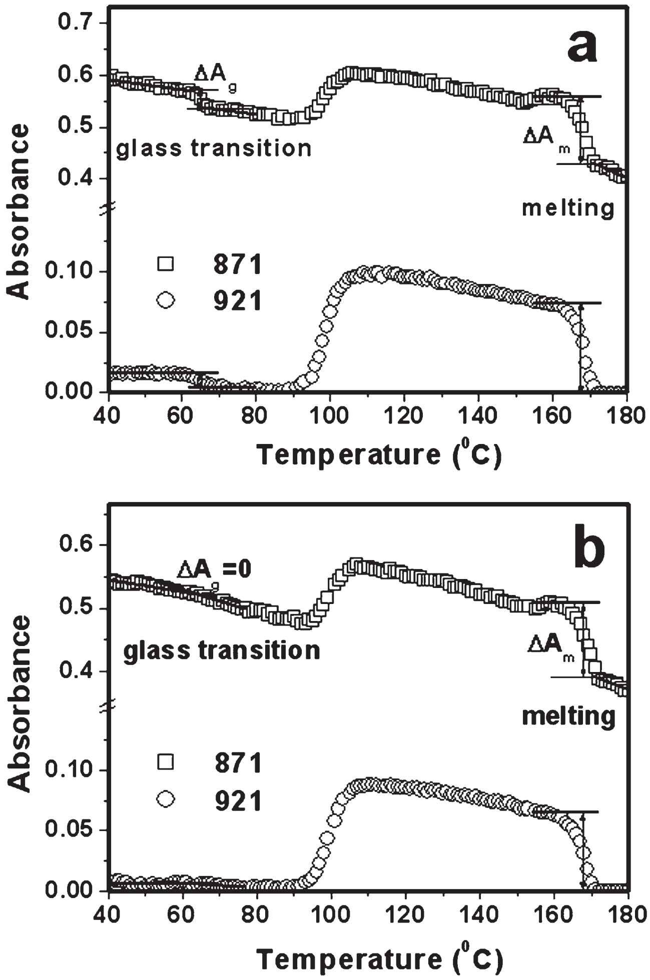

**Figure 3.** Temperature-dependent absorbance of indicated IR bands during a heating run of glassy PLLA aged for (a) 24 h and (b) 0 h.

volume recovery. Certainly, melting of local order must be accompanied by significant volume recovery, as the melting of crystals does.

To our knowledge, the enthalpic effect with respect to melting of crystals is mainly contributed by the disordering of intermolecular packing rather than by the coiling of molecular chains, which also holds true for the melting of ordered structures in the glass transition region.[8] In such a sense, the enthalpic effect $\Delta H_g$ from the DSC measurements during glass transition could be approximately correlated with the corresponding IR absorbance variation $\Delta A_g$ of 871 $cm^{-1}$ band, reflecting the change in the amount of ordered structures, through a relation of $\Delta A_g K_g = \Delta H_g$. Likely, this rule is applicable for the melting process, i.e., $\Delta A_m K_m = \Delta H_m$. Note that $K_g$ and $K_m$ are the order-dependent parameters for the glass and crystals, respectively. Thus, the relative order of the ordered structures in the glass to the crystals, $K_g/K_m$, can be estimated using

$$\frac{\Delta A_g K_g}{\Delta A_m K_m} = \frac{\Delta H_g}{\Delta H_m} \qquad (1)$$

Figure 4 shows the absorbance variation ratio $\Delta A_g/\Delta A_m$ of the 871 $cm^{-1}$ band and the enthalpy ratio $\Delta H_g/\Delta H_m$ and relative order $K_g/K_m$ deduced from eq1 during a heating run of PLLA aged for a desired period. As expected, at each aging period the value of $K_g/K_m$ is far below 1, suggesting that the ordered structure in the glass is less perfect than the crystals with long-range order. It is postulated that, as argued by other researchers,[8,9] paracrystalline type order or interchain cohesion with dense intermolecular packing seems to be created in the aged PLLA. On the other hand, the relative order $K_g/K_m$ is increased with aging time, as the glass transition temperature does (see Figure 1). Allowing that the $K_m$ could change little with aging time, deduced from nearly constant melting temperature of crystals, it means that during aging the formation of ordered structures in the glass is a kinetics-controlled event, and its internal molecular packing becomes denser and denser with aging time. Hence, melting of the ordered structure with denser intermolecular packing can give rise to shift of glass transition temperature to higher temperature, as observed in our case and other studies.[8,12−16]

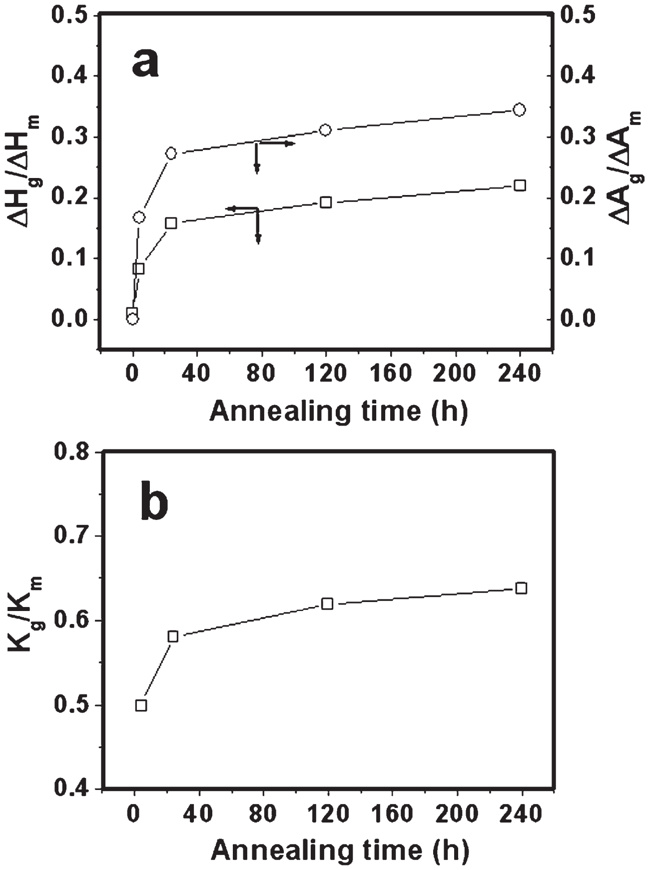

**Figure 4.** (a) Absorbance variation ratio (871 $cm^{-1}$ band) and enthalpy ratio and (b) the relative order of glass to crystals in the PLLA aged for a desired period.

**4. Conclusion.** In summary, during a heating run of aged glassy PLLA a sharp decrease in the absorbance of the IR bands related to intermolecular packing and helical sequence is observed in both glass transition region and melting process. This similarity strongly suggests that a local ordered structure with dense intermolecular packing, allowed by the coil−helix conformation transformation, does indeed prevail in the aged glassy PLLA, and its melting is the origin of the enthalpy recovery. Moreover, the local ordered structure in the aged glass is found to be less perfect than the crystals with long-range order, and its internal molecular packing is a kinetics-controlled event.

**Acknowledgment.** The financial support of this work was provided by the National Natural Science Foundation of China (No. 50973017 and 20704006) and the Project of Jiangxi Provincial Department of Education (No. GJJ08295).

## References and Notes

(1) Hutchinson, J. M. *Prog. Polym. Sci.* **1995**, *20*, 703–760.

(2) Roe, R. J.; Curro, J. J. *Macromolecules* **1983**, *16*, 428–434.

(3) Robertson, R. E.; Simha, R.; Currot, J. G. *Macromolecules* **1984**, *17*, 911–919.

(4) Heymans, N.; Dequenne, B. *Polymer* **2001**, *42*, 5337–5342.

(5) Bailey, N. A.; Hay, J. N.; Price, D. M. *Thermochim. Acta* **2001**, *367−368*, 425–431.

(6) McGonigle, E.; Daly, J. H.; Jenkins, S. D.; Liggat, J. J.; Pethrick, R. A. *Macromolecules* **2000**, *33*, 480–489.

(7) Soloukhin, V. A.; Brokken-Zijp, J. M.; van Asselen, O. L. J.; de With, G. *Macromolecules* **2003**, *36*, 7585–7597.

(8) Qian, R.; Shen, D.; Sun, F.; Wu, L. *Macromol. Chem. Phys.* **1996**, *197*, 1485–1493.

(9) Yeh, G. S. Y.; Geil, P. H. *J. Macromol. Sci., Phys.* **1967**, *1*, 235–249.

(10) McGonigle, E. A.; Daly, J. H.; Gallagher, S.; Jenkins, S. D.; Liggat, J. J.; Olsson, I.; Pethrick, R. A. *Polymer* **1999**, *40*, 4977–4982.

(11) Siegmann, A.; Geil, P. H. *J. Macromol. Sci., Phys.* **1970**, *4*, 239–271.

(12) Pan, P.; Zhu, B.; Inoue, Y. *Macromolecules* **2007**, *40*, 9664–9671.

(13) Aou, K.; Hsu, S. L.; Kleiner, L. W.; Tang, F. W. *J. Phys. Chem. B* **2007**, *111*, 12322–12327.

(14) Pyda, M.; Wunderlich, B. *Macromolecules* **2005**, *38*, 10472–10479.

(15) Mano, J. F.; Ribelles, J. L .G.; Alves, N. M.; Sanchez, M. S. *Polymer* **2005**, *46*, 8258–8265.

(16) Liao, K.; Quan, D.; Lu, Z. *Eur. Polym. J.* **2002**, *38*, 157–162.

(17) Sánchez, F. H.; Mateo, J. M.; Colomer, F. J. R.; Sánchez, M. S.; Ribelles, J. L. G.; Mano, J. F. *Biomacromolecules* **2005**, *6*, 3283–3290.

(18) Wolpert, S. M.; Weitz, A.; Wunderlich, B. *J. Polym. Sci., Polym. Phys.* **1971**, *9*, 1887–1905.

(19) Pan, P.; Liang, Z.; Zhu, B.; Dong, T.; Inoue, Y. *Macromolecules* **2008**, *41*, 8011–8019.

(20) Na, B.; Tian, N.; Lv, R.; Li, Z.; Xu, W.; Fu, Q. *Polymer* **2010**, *51*, 563–567.

(21) Zhang, J.; Duan, Y.; Sato, H.; Tsuji, H.; Noda, I.; Yan, S.; Ozaki, Y. *Macromolecules* **2005**, *38*, 8012–8021.

(22) Song, H. H.; Roe, R. J. *Macromolecules* **1987**, *20*, 2723–2732.