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Description	

Crystallization Behavior and Dynamic Mechanical Properties of Poly(L-Lactic Acid) with Poly(Ethylene Glycol) Terminated by Benzoate

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Abstract

Effect of the addition of poly(ethylene glycol) terminated by benzoate (PEG-BA) on the crystallization behavior and dynamic mechanical properties of poly(L-lactic acid) PLLA is studied as compared with poly(ethylene glycol) (PEG-OH). It is found that PEG-BA shows good plasticizing effect and the Flory-Huggins interaction parameter with PLLA is negative. Because PEG-OH having the same degree of polymerization is immiscible with PLLA, the end group in PEG-BA, *i.e.*, benzoate, plays an important role in the miscibility. Furthermore, PEG-BA does not induce the PLLA degradation at melt-processing, whereas PEG-OH leads to the hydrolysis degradation. Finally, the addition of PEG-BA pronounces the crystallization rate of PLLA at low crystallization temperatures and thus enhances the degree of crystallinity. Consequently, the temperature dependence of dynamic mechanical properties are similar to those of isotactic polypropylene.

Keywords: Poly(lactic acid); Plasticization; Crystallization; Hydrolysis degradation

Introduction

Poly(L-lactic acid) PLLA, as a biomass-based plastic, has received much attention nowadays because of its biodegradability and biocompatibility as well as high rigidity [1-3]. However, for a practical usage, considerable efforts will be further required to overcome the following defects; slow crystallization rate, poor melt elasticity [4], and mechanical brittleness.

Because of the slow crystallization rate, PLLA is hardly crystallized enough at conventional processing condition, which results in low heat distortion temperature. Therefore, numerous efforts have been carried out to enhance the crystallization rate of PLLA. One of the most famous methods is to add nucleating agents. It is well known that organo-silicated nano-clays act as good nucleating agents [5], which have been already employed in industry. Yamane and Sakai found that a small amount of poly(D-lactic acid) PDLA greatly enhances the crystallization rate of poly(L-lactic acid) PLLA, because stereocomplex crystallites having a higher melting point act as nucleating agents for the rest of PLLA melt [6]. Moreover, some organic compounds enhance the crystallization. Nam et al. found that *N*,*N*-ethylenebis(12-hydroxy stearamide) is a good nucleating agent for PLLA [7]. *N*,*N'*,*N"*-tricyclohexyl-1,3,5-benzenetricarboxamide is also known as a good nucleating agent, which improves the transparency of PLLA [8]. Furthermore, Kawamoto et al. evaluated a cycle time at injection-molding of PLLA with dibenzoylhydrazide compounds and found that it is shorter than 3 min at 110 ^{o}C of the mold temperature [9]. Yokohara and Yamaguchi clarified that poly(butylene succinate) PBS, that is immiscible with

PLLA [10], accelerates the crystallization of PLLA, which is pronounced when PBS exists in the fibrous shape [11,12]. Moreover, inorganic materials such as $CaCO_3$, $BaSO_4$, and TiO_2 also act as nucleating agents and enhance the crystallization rate of PLLA [13].

Besides nucleating agents, there is a great possibility to enhance the crystallization rate by the addition of plasticizers for a crystalline polymer having high glass transition temperature T_g, including PLLA, because the chain diffusivity, one of the important factors to decide the linear growth rate at crystallization, is enhanced especially in the temperature range near T_g. Up to now, a number of materials have been known as plasticizers for PLLA, such as poly(3-methyl-1,4-dioxan-2-one) [14], polyester-diol [15], citrate ester [16,17], triacetine [18,19], and poly(ethylene glycol) PEG [20-23]. Among these plasticizers, PEG has been studied for a long time. Sheth et al. firstly prepared blends of PLLA with PEG and found that PEG enhances the crystallization rate of PLLA. They also reported that the blends show biodegradability [21]. Hassouna et al. reported that the addition of PEG promotes PLLA degradation due to the hydroxyl groups in PEG, leading to poor mechanical properties [24]. Furthermore, Lai et al. evaluated the Flory-Huggins interaction parameter and found that it is negative, although they did not check the hydrolysis degradation of PLLA. They also studied the miscibility with PEG terminated by methyl groups [22].

In this study, the effect of the addition of PEG terminated by benzoate on the crystallization behavior and dynamic mechanical properties is investigated as compared with PEG having hydroxyl groups at the ends.

Experimental

Materials

The polymeric material used in this study was a commercially available poly(L-lactic acid) (PLLA) containing 1.1 % D-lactic acid. The number-average and weight-average molecular weights are 1.00×10^5 and 1.74×10^5, respectively.

Poly(ethylene glycol) terminated by benzoate (PEG-BA) was kindly prepared by New Japan Chemical from poly(ethylene glycol), which is referred to as PEG-OH. The average molecular weight of PEG-OH is 200. In this study, PEG-OH was also employed as a reference sample.

Sample preparation

The blends containing 10 and 20 wt% of a plasticizer were prepared by the solution blend technique in chloroform at room temperature. The weight fraction of PLLA and the plasticizer, *i.e.*, PEG-OH or PEG-BA, in the solution was 10 %. The solution was poured into a petri dish and left in a draft for 24 hours at room temperature to obtain a film. After being further dried in a vacuum oven at 80 ^{o}C for 4 hours, they were compressed into a flat film by a compression-molding machine (Tester sangyo, Table-type-test press SA-303-I-S) for 3 min at 200 ^{o}C and subsequently cooled at either 40 ^{o}C or 80 ^{o}C for 10 min. When the sample was cooled at 80 ^{o}C, it was subsequently plunged into an ice-water bath. The obtained films were stored at -20 ^{o}C to avoid further crystallization prior to the measurements.

Measurements

The number (M_n) and weight (M_w) average molecular weights of PLLA were evaluated by a gel permeation chromatography (GPC) (Tosoh, HLC-8020) with TSK-GEL GMHXL as a polystyrene standard. Chloroform was employed as eluant at a flow rate of 1.0 ml/min, and the sample concentration was 1.0 mg/ml.

Frequency dependence of oscillatory shear modulus G' and loss modulus G'' was evaluated at 190 ^{o}C using a cone-and-plate rheometer (TA Instrument, AR2000ex). The diameter and the cone angle are 25 mm and 4^{o}, respectively.

The linear growth rate of spherulites was examined at isothermal crystallization using a polarized optical microscope (Leica, DMLP) equipped with a hot-stage (Mettler, FP90). After heating up to 210 ^{o}C, the sample was cooled down to various crystallization temperatures at a cooling rate of 20 ^{o}C/min.

Temperature dependence of tensile storage modulus E' and loss modulus E'' was measured using a rectangular specimen with 5 mm in width, 25 mm in length and 0.4 mm in thickness by a dynamic mechanical analyzer (UBM, Rheogel E4000-DVE) in the temperature range between -100 and 170 ^{o}C. The heating rate was 2 ^{o}C/min, and the applied frequency was 10 Hz.

Thermal analysis was conducted by a differential scanning calorimeter (DSC) (Mettler, DSC820^{e}) under a nitrogen atmosphere. The samples were heated from room temperature to 210 ^{o}C at a heating rate of 10 ^{o}C/min. The amount of the samples in an aluminum pan was approximately 10 mg.

Results and Discussion

Thermal Stability and Rheological Properties

According to Hassouna [24], poly(ethylene glycol) leads to the hydrolysis degradation of PLLA. Therefore, the molecular weight is examined prior to the measurements of the rheological and thermal properties using film samples prepared by the compression-molding.

Fig. 1

Fig. 1 shows the GPC curves as a polystyrene standard. There are two peaks in the blend samples, which are ascribed to PLLA and the plasticizer. As seen in the figure, PEG-OH induces the degradation of PLLA as reported previously [24]. The M_n and M_w of PLLA in the blend containing 10 wt% of PEG-OH are 4.30×10^4 and 8.31×10^4, respectively, whereas those of pure PLLA are almost the same as those of the pellet even after the compression-molding. Considering that PLLA in the solution-cast film of the blend has the same molecular weight as the pure PLLA (but not presented), the hydrolysis degradation occurs by the thermal history at the compression-molding. In contrast, the GPC curve of PLLA in the blend with PEG-BA is unchanged. The M_n and M_w of PLLA in PLLA/PEG-BA (90/10) are 9.72×10^4 and 1.70×10^5, respectively, which are almost the same as those of the pure PLLA.

The decrease in the molecular weight of PLLA by PEG-OH is clearly detected also by the rheological properties. As shown in Fig. 2(a), both moduli decrease greatly with the addition of PEG-OH. The zero-shear viscosity η_0 of PLLA/PEG-OH (90/10) is calculated to be 40 Pa s, whereas that of pure PLLA is 450 Pa s. Considering that η_0 is proportional to $M_w^{3.4}$, the value is appropriate.

Fig. 2

As seen in Fig. 2(b), the moduli decrease slightly with the addition of PEG-BA. It is found that η_0 of PLLA/PEG-BA (90/10) is 310 Pa s. According to Graessley [25], η_0 of a solution is given by the relation.

$$\eta_0(\phi) \propto \xi_0(\phi)\phi^{3.6} \qquad \text{(eq. 1)}$$

where ϕ is the volume fraction of a polymer and ξ_0 is the monomeric friction coefficient. The equation corresponds to the original Berry-Fox formula [26]. Assuming that ξ_0 is not affected by PEG-BA, η_0 predicted by the equation (306 Pa s) agrees well with the experimental value.

It is also found from the figures that the steady-state compliances J_e^0 are calculated to be 3.7×10^{-5} Pa^{-1} and 3.4×10^{-5} Pa^{-1} for pure PLLA and PLLA/PEG-BA (90/10), respectively. Therefore, the weight-average relaxation times τ_w, calculated by the product of η_0 and J_e^0, are found to be 1.7×10^{-2} s and 1.0×10^{-2} s for pure PLLA and PLLA/PEG-BA (90/10), respectively.

Linear growth rate of spherulites

Fig. 3 exemplifies the spherulite texture observed under cross polars with a full-wave plate for PLLA and the blends with PEG-BA. A typical Maltese-cross pattern, showing negative spherulites, is detected for all samples, although PLLA/PEG-BA (80/20) shows slightly disturbed texture.

Fig. 3

The growth curves of the spherulite radius at various crystallization temperatures T_c for PLLA PLLA/PEG-BA (80/20) are shown in Fig. 4. It is found that the spherulite radius increases linearly with the crystallization time, indicating that the PLLA concentration in the molten region at the front of spherulites is a constant. The result suggests that the diffusion rate of PEG-BA is lower than the linear growth rate of PLLA spherulites. Since the plasticizer molecules are not incorporated into the crystalline lattice of PLLA, they exist in the amorphous region between lamellae.

The slope of the lines in Fig. 4 represents the linear growth rate G as follows;

$$G = \frac{dR}{dt} \qquad \text{(eq. 2)}$$

where R is the radius of spherulites.

Fig. 4

Fig. 5 shows the relation between G and T_c. As seen in the figure, pure PLLA shows a maximum around at 130 ^{o}C.

Fig. 5

According to Miyata and Masuko [27], the crystallization temperature at which G shows a maximum, $T_{c\text{-}max}$, is given by

$$T_{c-\max} = \frac{T_g + T_m^0}{2} \qquad \text{(eq. 3)}$$

where T_m^0 is the equilibrium melting point.

Since T_g of PLLA is 58 ^{o}C [28] and T_m^0 is 207 ^{o}C [29], $T_{c\text{-}max}$ is expected to be 132.5 ^{o}C. This corresponds with the experimental result.

Furthermore, it is found that G is greatly enhanced especially at low T_c by the addition of the plasticizer. The location of the peak shifts to lower T_c owing to the decrease in T_g. Because actual processing is often carried out using water as a cooling medium, the shift of $T_{c\text{-}max}$ to a lower temperature will be a great benefit in industries. On the contrary, G at high T_c decreases with increasing PEG-BA, suggesting that T_m^0 decreases with PEG-BA. In other words, the Flory-Huggins interaction parameter between PLLA and PEG-BA is negative.

Dynamic Mechanical Properties

Fig. 6 shows the temperature dependence of the dynamic mechanical properties for the samples cooled at 40 ^{o}C. As seen in the figure, the tensile storage modulus E' of PLLA falls off sharply at 65 ^{o}C owing to the glass-to-rubber transition. Correspondingly, the loss modulus E'' shows a distinct peak. Beyond T_g, both moduli increase with temperature in the range between 85 and 95 ^{o}C. This is attributed to the cold crystallization, which is often observed for a crystalline polymer with slow crystallization rate. The phenomenon demonstrates that the degree of crystallization of the initial sample cooled at 40 ^{o}C is considerably low. Because of the low degree of crystallinity, the heat distortion temperature is determined by T_g. The cold-crystallization behavior is also detected for the plasticized samples, although both T_g and the cold crystallization temperature are located at lower temperatures. The results indicate that the cooling condition, *i.e.*, 40 ^{o}C for 10 min, is not sufficient enough to crystallize. Moreover, double peaks are detected in the *E"* curve for PLLA/PEG-OH (90/10), demonstrating that they are immiscible. On the contrary, only a single peak is detected for PLLA/PEG-BA (90/10). The results suggest that the end group of poly(ethylene glycol) plays an important role in the miscibility with PLLA.

Fig. 6

Fig. 7 shows the dynamic mechanical spectra for the samples cooled at 80 ^{o}C for 10 min. It is demonstrated that both plasticized samples show monotonical decrease in the *E'* curve with temperature, although pure PLLA exhibits the cold crystallization behavior. It suggests that the cooling condition, *i.e.,* 80 ^{o}C for 10 min, allows PLLA to crystallize greatly for the plasticized samples. The figure also shows that the *E"* peak of the plasticized samples is broader and weaker than that of pure PLLA. This is reasonable because the crystallization reduces the amorphous region and broadens the characteristic times of the relaxation of amorphous chains. Moreover, the *E"* peak at -80 ^{o}C for PLLA/PEG-OH (90/10), ascribed to T_g of PEG-OH, is more pronounced than that in Fig.6. The small amount of amorphous PLLA, as a result of enhanced crystallization, accelerates the phase separation in the amorphous region. On the contrary, it is found that PEG-BA shows good miscibility with PLLA even after the crystallization of PLLA.

Fig. 7

Thermal Properties

The DSC heating curves are shown in Fig. 8. The arrows in the figure denote T_g of pure PLLA.

Fig. 8

It is found from Fig. 8(a) that a sharp exothermal peak ascribed to cold crystallization is detected beyond T_g for the samples cooled at 40 ^{o}C, corresponding to the dynamic mechanical spectra. In the case of the blends with PEG-BA, the exothermic peaks are located at lower temperatures owing to the low T_g. The crystalline nucleus of PLLA produced at processing may also be responsible for the prompt crystallization at the heating process. On the contrary, the exothermic peak is not observed for the plasticized samples cooled at 80 ^{o}C as shown in Fig. 8(b).

The degree of crystallinity for PLLA χ is determined by eq. 4;

$$\chi(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_{100\%}} \times 100 \qquad \text{(eq. 4)}$$

where ΔH_m the heat of fusion, ΔH_c the exothermic heat at cold crystallization, and $\Delta H_{100\%}$ the heat of fusion for a perfect PLLA crystal (93.1 J/g) [30].

Table 1

Table 1 shows the crystallinity of PLLA with various amounts of PEG-BA or PEG-OH. It is found that the degree of crystallinity increases with the amount of the plasticizers. The plasticized samples cooled at 80 ^{o}C show high level of crystallinity, *i.e.*, 39 – 47 %. As a result, *E’* decreases monotonically with temperature without abrupt drop. Because the dynamic mechanical spectra for the plasticized samples cooled at 80 °C are similar to those of conventional isotactic polypropylene (i-PP), the blends have a great possibility to be replaced from i-PP.

Conclusions

Crystallization behavior and thermal and dynamic mechanical properties for plasticized PLLA are studied employing PEG having benzoate groups at chain ends (PEG-BA). The hydrolysis degradation of PLLA, which is a severe problem at thermal processing, is not induced by the addition of PEG-BA, whereas the addition of a conventional PEG having hydroxyl groups at chain ends (PEG-OH) accelerates the hydrolysis degradation. The Flory-Huggins interaction parameter between PLLA and PEG-BA is found to be negative, although PEG-OH is immiscible with PLLA. Furthermore, the linear growth rate of PLLA crystallization is greatly enhanced especially at low temperatures because of the decrease in T_g as well as the pronounced molecular mobility of PLLA chains due to the decrease in entanglement couplings. The enhanced crystallization rate affects the mechanical and thermal properties. Because of the high degree of crystallinity, which is obtained, *e.g.,* at 80 °C for 10 min as a cooling condition, the cold crystallization behavior is not observed at the measurements of thermal and dynamic mechanical properties. Consequently, the tensile modulus gradually decreases with temperature. Since the dynamic mechanical spectra are similar to those of i-PP, the heat distortion temperature will be greatly improved.

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Figure Captions

Fig. 1 GPC curves of (top) PLLA, (center) PLLA/PEG-OH (90/10), and (bottom) PLLA/PEG-BA (90/10) films prepared by the compression-molding.

Fig. 2 Frequency dependence of oscillatory shear moduli such as (circles) storage modulus G' and (diamonds) loss modulus G'' at 190 ^{o}C; (a) (closed) pure PLLA and (open) PLLA/PEG-OH (90/10); (b) (closed) pure PLLA and (open) PLLA/PEG-BA (90/10).

Fig. 3 Spherulite texture for (a) pure PLLA, (b) PLLA/PEG-BA (90/10) and (c) PLLA/PEG-BA (80/20) during isothermal crystallization at 120 ^{o}C.

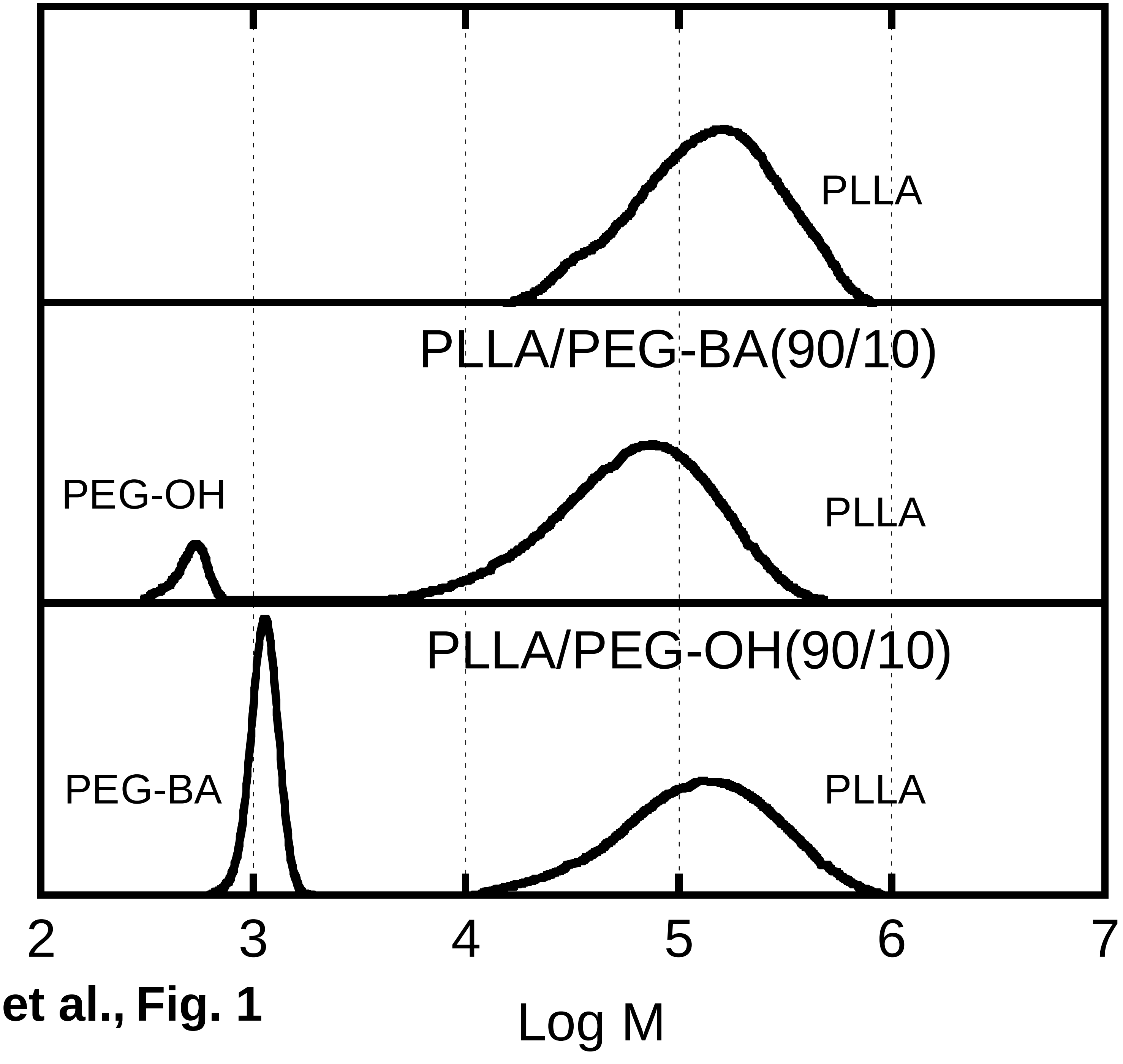
Fig. 4 Growth curves of spherulite radius R for PLLA/PEG-BA (80/20) at various crystallization temperatures T_c.

Fig. 5 Linear growth rate of spherulites G versus crystallization temperature T_c for (closed circles) pure PLLA, (open diamonds) PLLA/PEG-BA (90/10), and (open triangles) PLLA/PEG-BA (80/20).

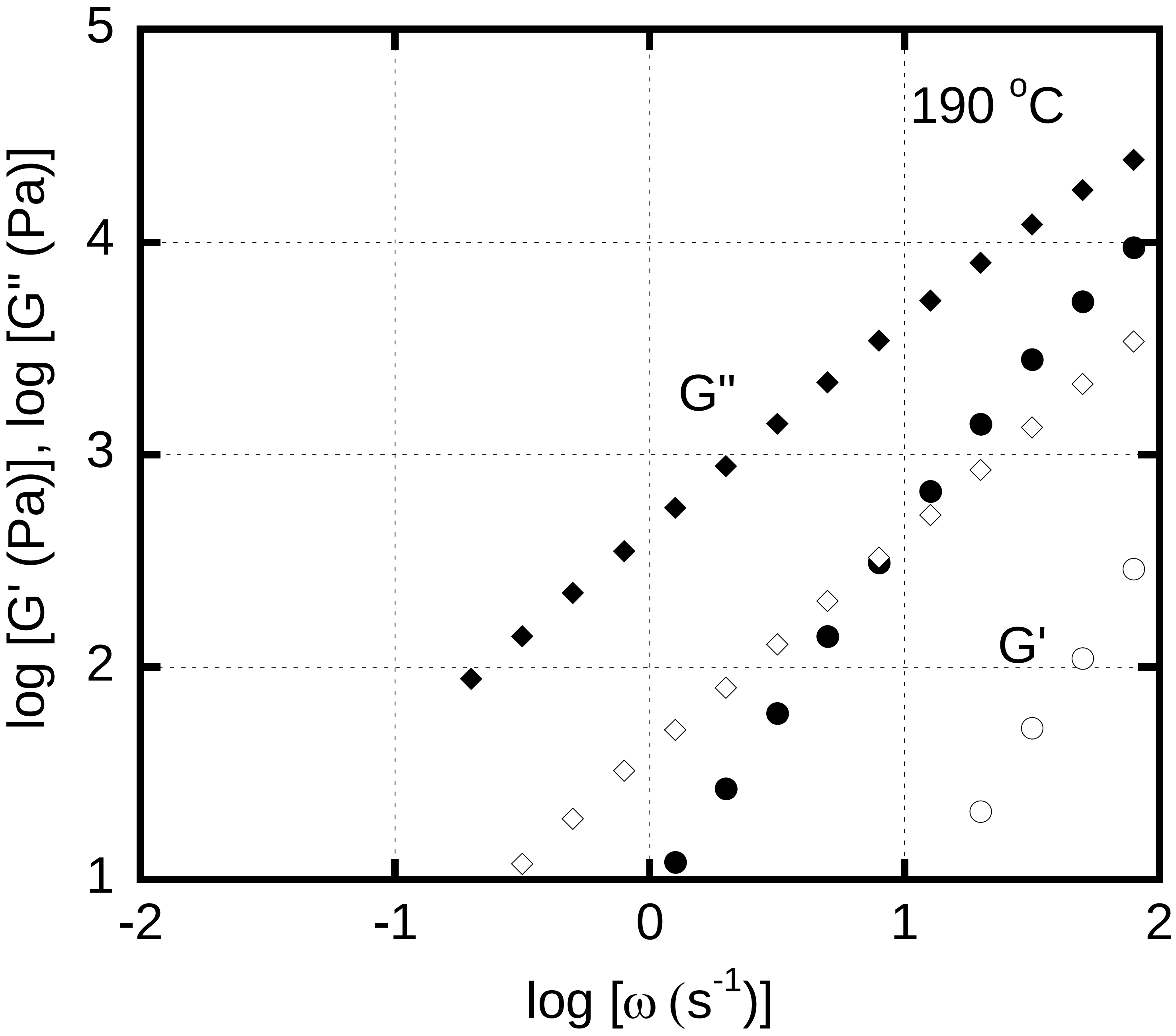
Fig. 6 Temperature dependence of tensile storage modulus E' and loss modulus E'' at 10 Hz for the samples cooled at 40 ^{o}C: (circles) pure PLLA, (diamonds) PLLA/PEG-BA (90/10), and (triangles) PLLA/PEG-OH (90/10).

Fig. 7 Temperature dependence of tensile storage modulus *E'* and loss modulus *E"* at 10 Hz for the samples cooled at 40 °C: (circles) pure PLLA, (diamonds) PLLA/PEG-BA (90/10) and (triangles) PLLA/PEG-OH (90/10).

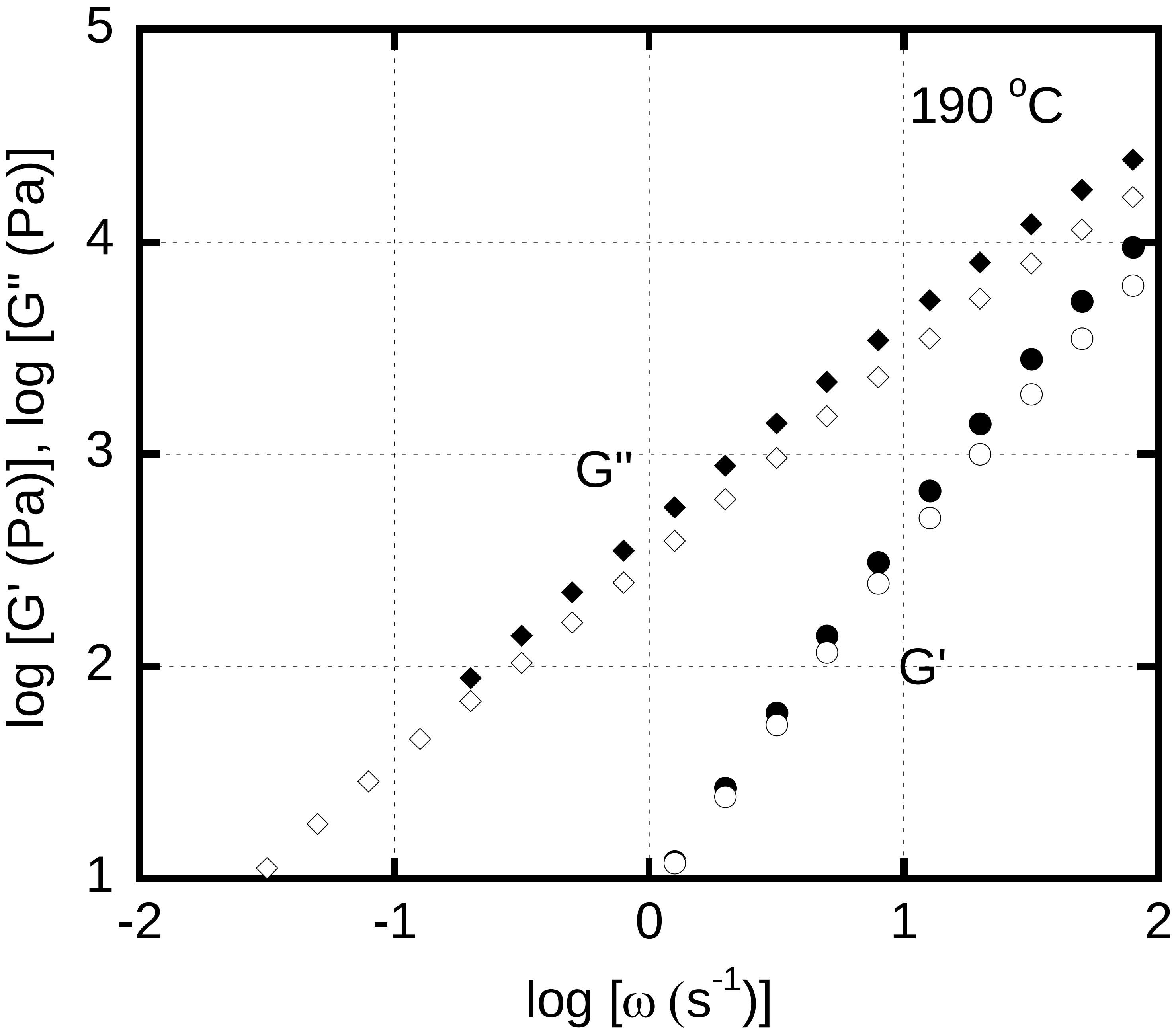
Fig. 8 DSC heating curves for PLLA, PLLA/PEG-BA (90/10) and PLLA/PEG-BA (80/20) cooled at (a) 40 °C and (b) 80 °C.



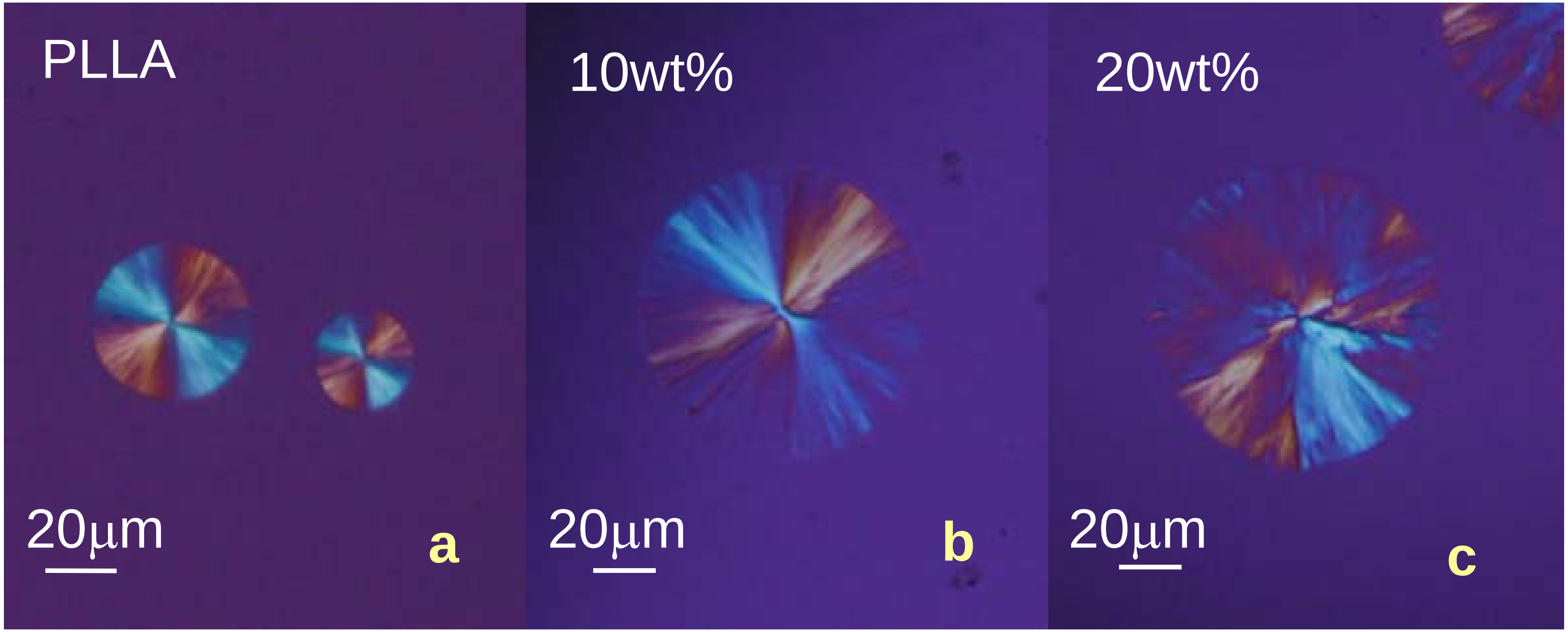
Huang et al., Fig. 1



Huang et al., Fig. 2(a)



Huang et al., Fig. 2(b)



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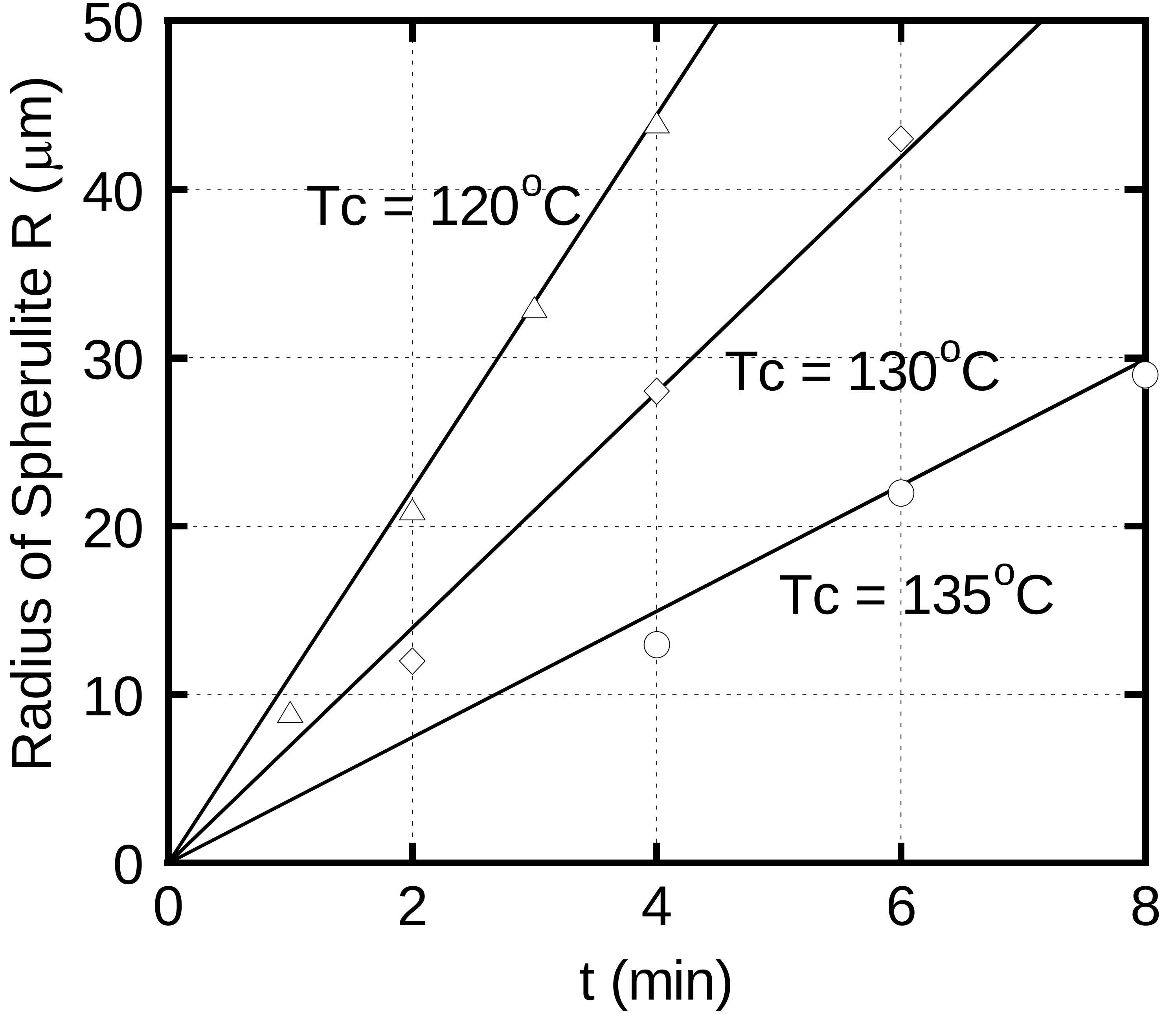

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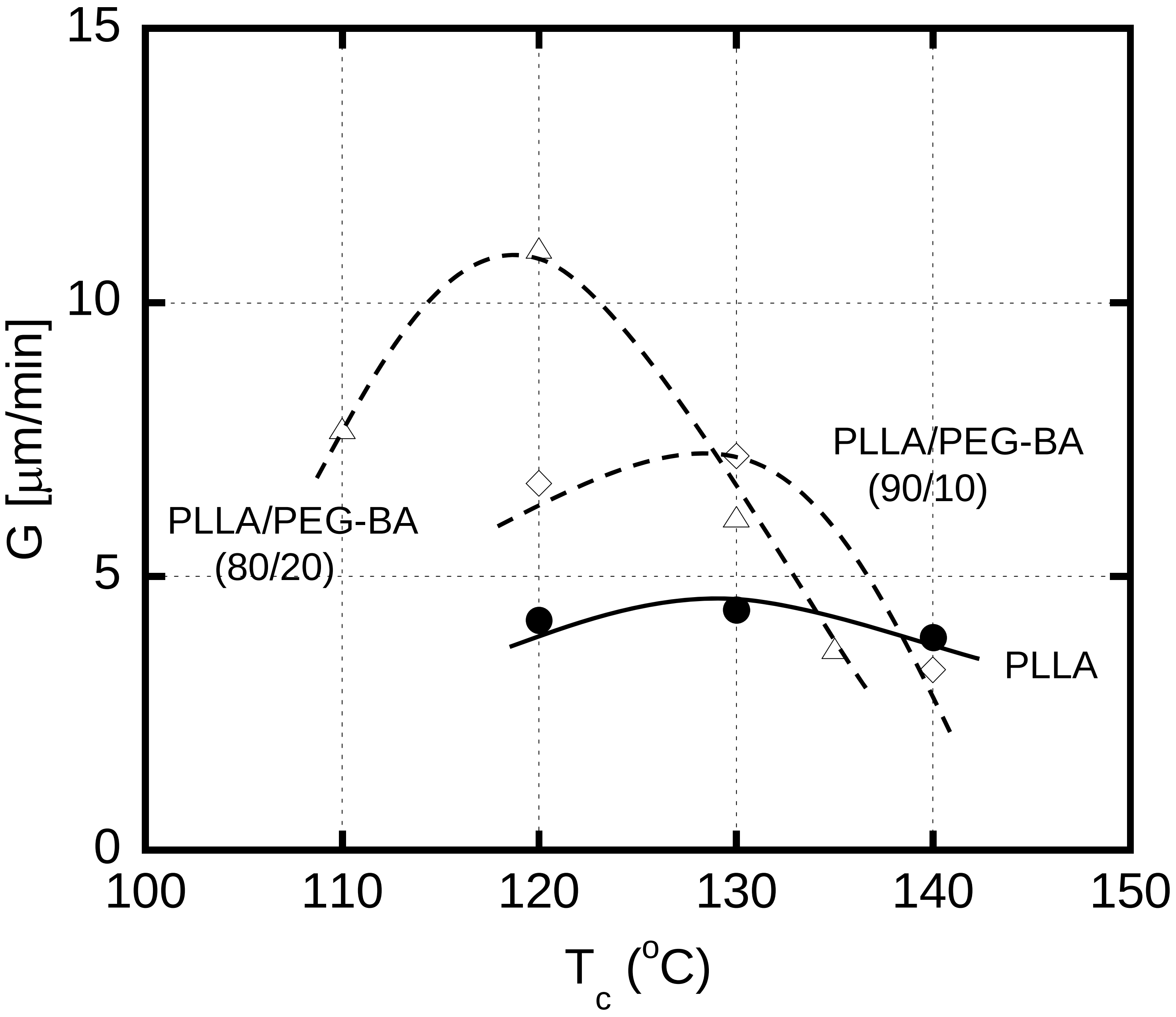

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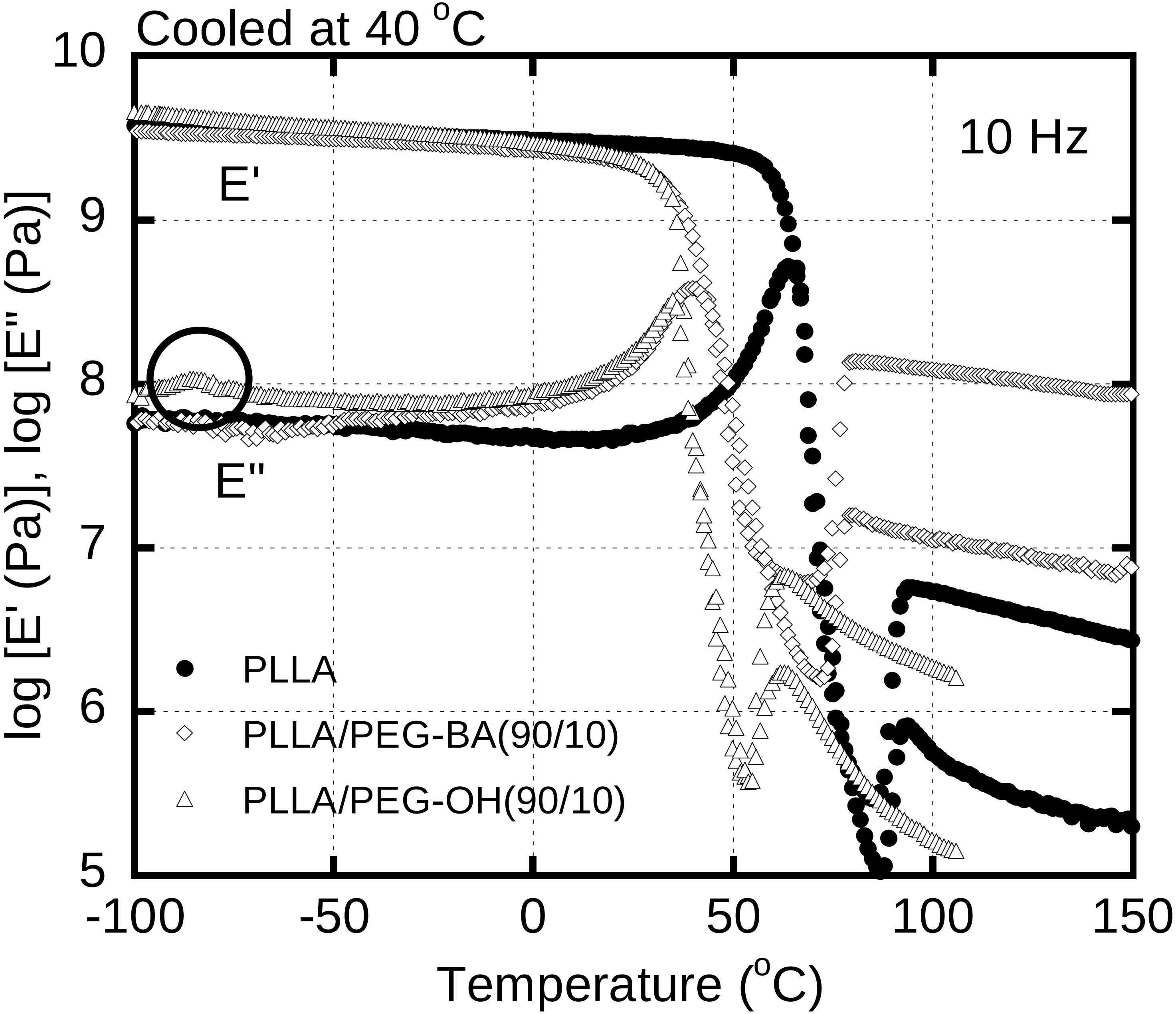

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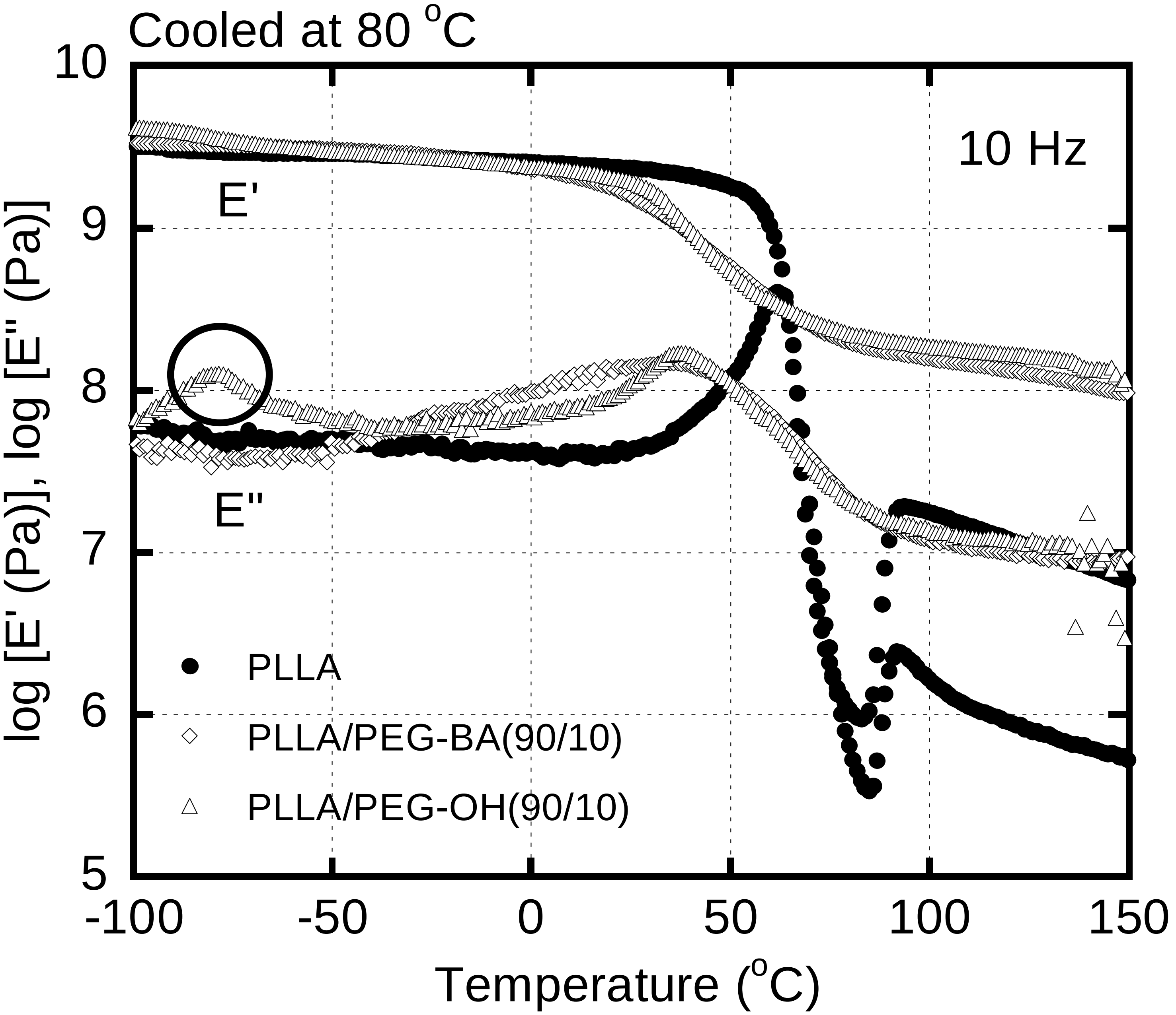

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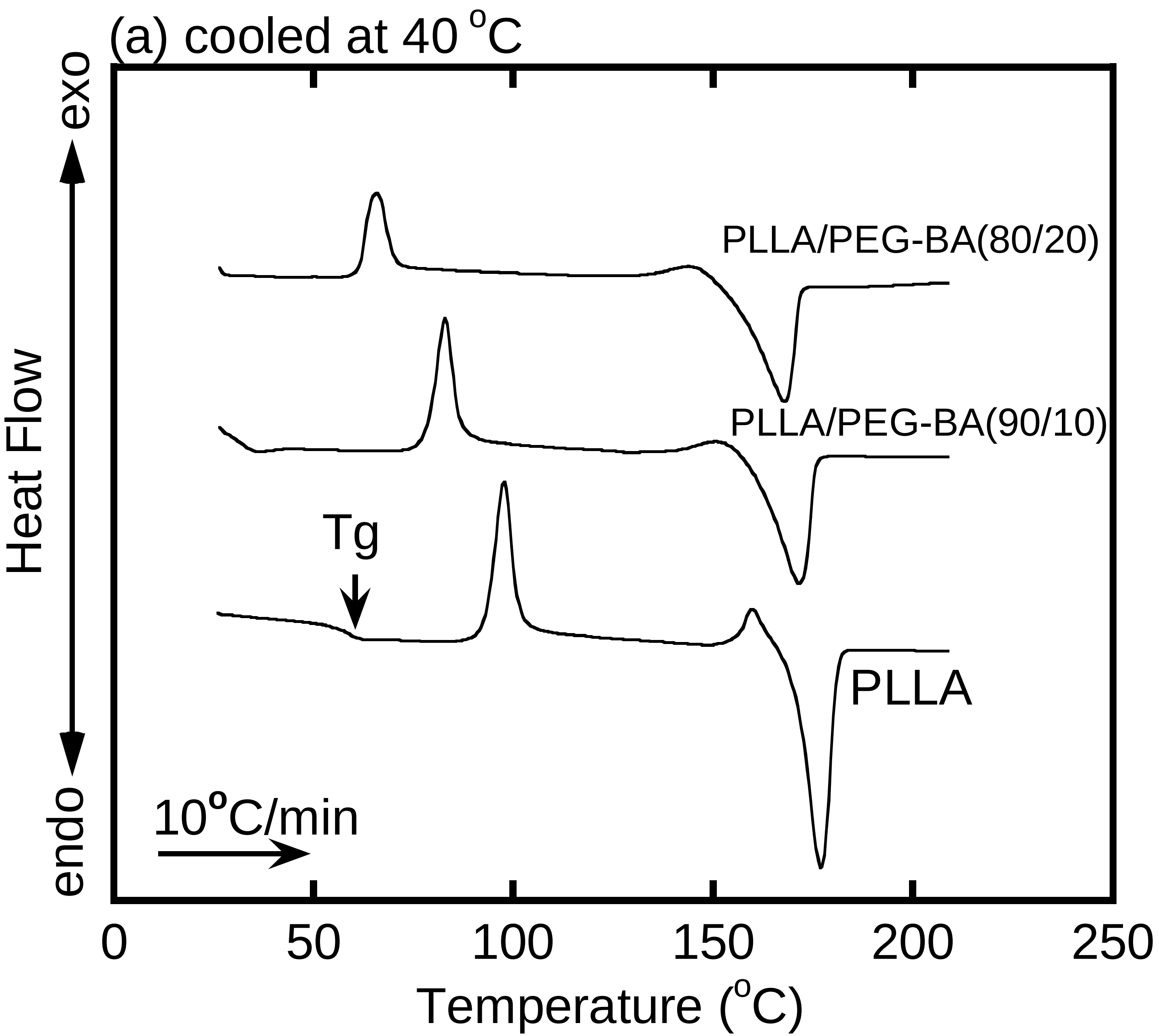
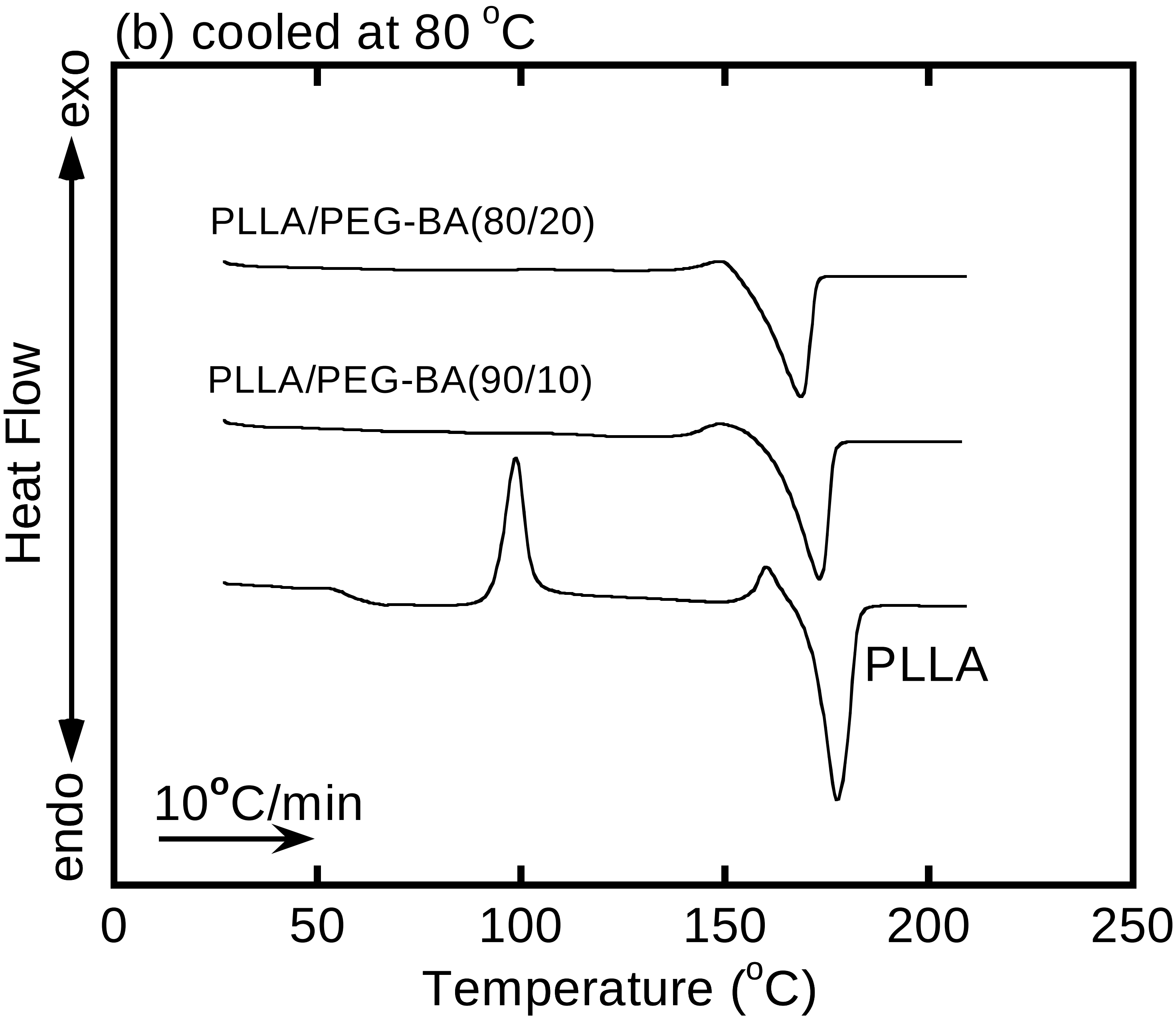


Huang et al., Fig. 8(a)



Huang et al., Fig. 8(b)

Table 1 Thermal properties and crystallinity of the sample films

Plasticizer	Content (wt%)	Mold Temperature [^{o}C]	T_g [^{o}C]	T_m [^{o}C]	Crystallinity [%]
-	0	40	64	178	12
PEG-BA	10		40	172	17
PEG-BA	20		25	168	25
PEG-OH	10		35	169	29
PEG-OH	20		34	163	33
-	0	80	63	177	16
PEG-BA	10		31	173	39
PEG-BA	20		-23	168	42
PEG-OH	10		36	170	47
PEG-OH	20		41	165	47