Determination of M-H-S Parameters for Estimation of PLLA Chemical Recycling

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INTRODUCTION Poly(L-lactic acid) (PLLA) had been received much interest in medical and pharmaceutical fields, because of its biodegradability, but nowadays it has been applied in a wide field, such as electro/electronics devices, parts of automobile, food packages, etc., due to its biomass origin. PLLA also has attracted the attention of many researchers because of its superior recyclability to raw materials, i.e., L-lactic acid, L,L-lactide, and oligomers.

To achieve the recycling precisely, accurate evaluation of molecular weight and molecular weight distribution values of resultants in degradation processes is indispensable. The number and weight-average molecular weights of polymers are conveniently and widely evaluated with the size-exclusion chromatography (SEC), resulting in calculation as relative values based on polystyrene standards. More accurate molecular weights values are given by using the universal calibration method (UCM)[1], which utilizes a relationship between the molecular weight and the hydrodynamic volume. The UCM, which needs the Mark-Houwink-Sakurada (MHS) parameters: K and a, gives close molecular weight values to exact ones determined by other evaluation method, e.g. osmotic pressure and light scattering measurements.

Recently, the process temperature for SEC analysis has become set at 40°C to avoid the influence of surrounding temperatures. However, so far, no MHS parameters for PLLA and polystyrene at 40°C have been reported, while there are many parameters measured at 25-35 °C. When the molecular weight of PLLA was calculated tentatively using the MHS parameters measured at different temperatures, it was obvious that the resulting tentative values showed a certain extent of errors if compared with the molecular weights evaluated with proper MHS parameters.

In order to correct this incongruity in the molecular weight evaluation and use more exact molecular weight estimated by UCM, in this study, the MHS parameters of PLLA and polystyrene at 40°C were measured in chloroform and THF solution using viscometry and a triple detector (RI, capillary viscometer, and RALLS) system. The MHS parameters measured at 40°C will be used for evaluations of various kinetics parameters of PLLA.

EXPERIMENTAL Four PLLA samples with polydispersity indices (PDIs) of around unity were purchased from Polymer Source, Inc. Two PLLA samples with PDIs of around two were prepared by high-pressure steam hydrolysis and following fractional precipitation. Polystyrene (PS) standard samples were obtained from TOSOH Corp.

Viscosity of the samples were measured in chloroform and THF for PLLA and in chloroform for PS using Ubbelohde viscometer in a thermostated water bath at 40±0.1°C. Intrinsic viscosities of the samples were obtained by the extrapolation of the plots of the inherent and reduced viscosities against concentration of samples.

The relative molecular weights of PLLA samples were analyzed on a TOSOH HLC-8120 GPC system at 40°C using TOSOH TSKgel Super HM-H column and chloroform eluent (0.6 mL min^{-1}). PS standards with M_n values from 5.0×10^2 to 1.11×10^6 were used for

calibration.

RESULTS and DISCUSSION

The MHS parameters in THF at 40°C were determined using a PLLA sample (M_n 71 000, M_v 120 000, M_w 130 000) on a triple detector TDA-302 system (Viscotek. Corp.). The measured data were analyzed by an Omnisec 4.5 software, resulting in $K=3.57\times10^{-4}$ dL·g^{-1} and $a=0.70$ (Table 1). The viscosity-average molecular weights of other PLLA samples were calculated from intrinsic viscosity values measured at 40°C in THF based on the MHS parameters determined in THF.

Fig1. Intrinsic viscosity (dL/g) versus viscosity-average molecular weight for PLLA (▲)and polystyrene (■)in chloroform

Table 1. M-H-S parameters for PLLA and PS

Polymer	PLLA		PS
solvent	CHCl$_3$	THF	CHCl$_3$
K ($\times10^4$ dL/g)	2.48	3.57	2.07
a	0.72	0.70	0.65

To estimate the MHS parameters of PLLA at 40°C in chloroform, the intrinsic viscosity values of PLLA and PS samples were measured in a similar manner with the measurement in THF. Figure 1 shows the viscosity-molecular weight relationships of PLLA and PS in chloroform at 40°C. The linear relationships were represented with high accuracy in both cases. The MHS parameters were estimated from the plots and summarized in Table 1. The a values were in a range of 0.65 to 0.72, indicating that chloroform was good solvents for both polymers. The K value 2.48 dL·g^{-1} of PLLA decreased by 2.97 from 5.45 dL·g^{-1} at 30 [2], while in the case of PS, the K value increased from 0.49 to 2.07 dL·g^{-1}, suggesting different changes in chain variation tendency between PLLA and PS with temperature.

To clarify influences of the MHS parameters on molecular weight calculation, PLLA sample (exact M_v 120 000) was employed to calculate the molecular weight by UCM, resulting in M_v = 88 000 and 122 000 at 30 and 40°C, respectively. Obviously, the M_v value calculated by using the proper MHS parameters was nearly close to the exact value. Moreover, these values were below the half of a conveniently calculated relative value M_n 99 000 and M_w 255 000 based on polystyrene standards.

Similar results were obtained in comparisons using hydrolyzed PLLA samples in a M_w range of 3 000~75 000. Molecular weights of the samples calculated using the parameters at 40°C were in range of 0.5 to 0.7 when expressed as ratios against the relative molecular weights based on polystyrene standards. These ratios were different from the ratios in a range of 0.3 to 0.5 when previously reported MHS parameters measured at 25~35 °C were used.

CONCLUSION It was clearly illustrated that to precisely evaluate the molecular weight of PLLA, UCM using appropriate MHS parameters gives nearly close to exact molecular weight values, which will enable us to control the chemical recycling of PLLA.
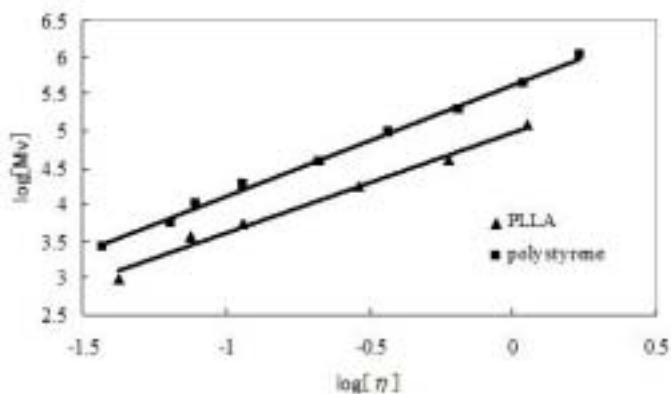
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