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Molecular weight distribution and branched structure of biodegradable aliphatic polyesters determined by s.e.c.–MALLS

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Molecular weight distribution and mean square radius as a function of molecular weight for biodegradable aliphatic polyesters have been measured by multiangle laser light scattering (MALLS) detector for size exclusion chromatography (s.e.c.). The difference of their molecular structures is discussed in relation to the melt elasticity, which contributes to processability for extrusion coating and extrusion foaming. The evaluated values of branching ratio indicate the existence of long chain branched structures.

(Keywords: s.e.c.–MALLS; aliphatic polyester; long chain branching)

Introduction

Biodegradable plastics have been considered as a possible solution for the ecological and environmental problems of the huge amount of plastic waste. Some biodegradable polymer materials, for example polysaccharides and aliphatic polyesters, are manufactured commercially. However, these materials are not in common use yet, because of their high cost and limited applicability. Further investigation and development are required.

The processability to be applied to conventional forming methods must be an important factor to extend the use of biodegradable plastics. Biodegradable aliphatic polyesters of high molecular weight, consisting of dihydric alcohols and dicarboxylic acids, have been developed by Showa Highpolymer Co. and Showa Denko K.K., trade name Bionolle. These materials are suitable for various processing methods, such as film blowing, blow moulding, extrusion coating and extrusion foaming as well as polyethylene[1]. From this point of view, not only their chemical structures but also their molecular structures become important subjects to improve their adaptability.

The light scattering experiment on polymer solutions is one of the basic methods to characterize molecular weight and molecular radius of the polymer. However, some technical difficulties restricted its application to on-line measurements within the monoangle light scattering detector. Recently the multiangle laser light scattering (MALLS) detector, which is able to measure light scattering intensities of various scattering angles at the same time, has been developed[2]. This detector connected with size exclusion chromatography (s.e.c.) makes it possible to determine actual molecular weight distribution and molecular size distribution of polymer without any equivalence.

In this study, molecular weight distribution and mean square radius as a function of molecular weight of Bionolle polymers are evaluated by means of s.e.c.–MALLS. Then an indication of their branched structures is considered in relation to their processability.

Experimental

Three types of Bionolle were selected; their grade numbers were 1001, 1903 and 1003V2. While grade 1001 was made as a linear type consisting of bifunctional monomers, grades 1903 and 1003V2 were produced as branched types by copolymerization with additional monomers including multifunctional groups[3]. Their values of melt flow rate (m.f.r.) at 190°C by means of JIS K-7210 are listed in *Table 1*. Their values of m.f.r. were around 4 g/10 min. Samples for s.e.c.–MALLS were prepared by precipitation from their chloroform solutions into excess amounts of methanol in order to remove their additives. The precipitated polymers were filtered and dried in a vacuum at room temperature.

For an s.e.c.–MALLS eluent, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was selected because of its good solubility and relatively large differential refractive index for polyesters. The eluent contained ammonium acetate of 15 mM concentration in order to have a reasonable chromatogram[4,5]. The eluent with the salt was filtered by membrane filter with 0.2 μm pores prior to s.e.c.–MALLS measurement.

Differential refractive index of the Bionolle solutions was measured by using Milton Roy Co. KMX-16 at 25°C. The solvent was the same as that for s.e.c.–

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Table 1 Resin properties and molecular characteristics

Grade	Melt flow rate[a] (g/10 min)	Swell ratio	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$M_z \times 10^{-4}$	M_w/M_n	M_z/M_w	g_m
1001	2.7	1.4	4.7	14	31	3.0	2.2	—
1903	4.3	2.5	2.4	22	120	9.2	5.5	0.82
1003V2	4.0	1.7	2.7	17	100	6.3	5.9	0.88

[a] JIS K-7210 condition 4 (190°C, 2.16 kg load)

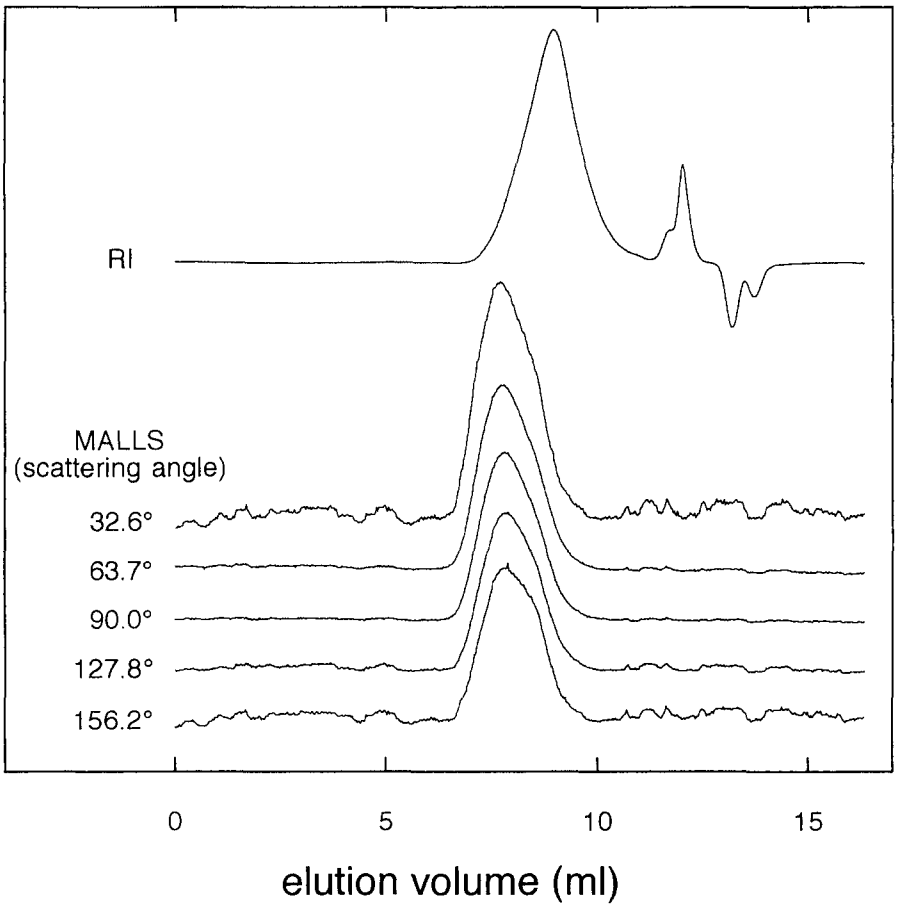

Figure 1 S.e.c. chromatograms by r.i. and MALLS detectors for grade 1003V2. The numbers represent the light scattering angles

MALLS. A Shodex s.e.c. system (DEGAS, DS-4 pump and AO-50 oven) was used with a Shodex HFIP-806M column. A refractive index (r.i.) detector (Shodex SE-51) was employed to determine the fraction concentration. For this purpose, the r.i. constant was evaluated by using a solution of a low molecular weight poly(tetramethylene succinate). Wyatt Technology Co. DAWN DSP-F was connected to it as a MALLS detector. S.e.c.–MALLS measurements were made at 25°C.

All analyses of s.e.c.–MALLS data were made by Wyatt Technology Co. ASTRA, the software for this experimental method. Values of 1.276 as refractive index of HFIP and 0.177 ml g^{-1} as differential refractive index of HFIP solution of the sample polyesters at 25°C were used. The second virial coefficient (A_2) was neglected in this study. Although contributions of A_2 to the values of molecular weight and mean square radius would be little, probably less than 10%, the evaluation of A_2 by means of a static light scattering method remains to be done in further studies. Molecular weight and mean square radius of the polymer in each s.e.c. fraction were determined by means of Zimm plot analysis with first order fit.

Results and discussion

Grades 1001, 1903 and 1003V2 have almost the same m.f.r. values as listed in *Table 1*. However, they show different processability, particularly for extrusion coating and extrusion foaming. In these fabrications, melt elasticity plays an important role. In order to compare elasticity of polymer melts, die swell is often measured. A high value of swell ratio, defined as the ratio of extrudate diameter to capillary die diameter, consists in high elasticity. *Table 1* contains swell ratio in the m.f.r. measurement for each sample. Grade 1903 has the largest value of swell ratio, and shows the best processability for extrusion coating and extrusion foaming among them.

The difference of melt elasticity is attributed to molecular structures. Especially, molecular weight distribution has a great influence on the viscoelasticity

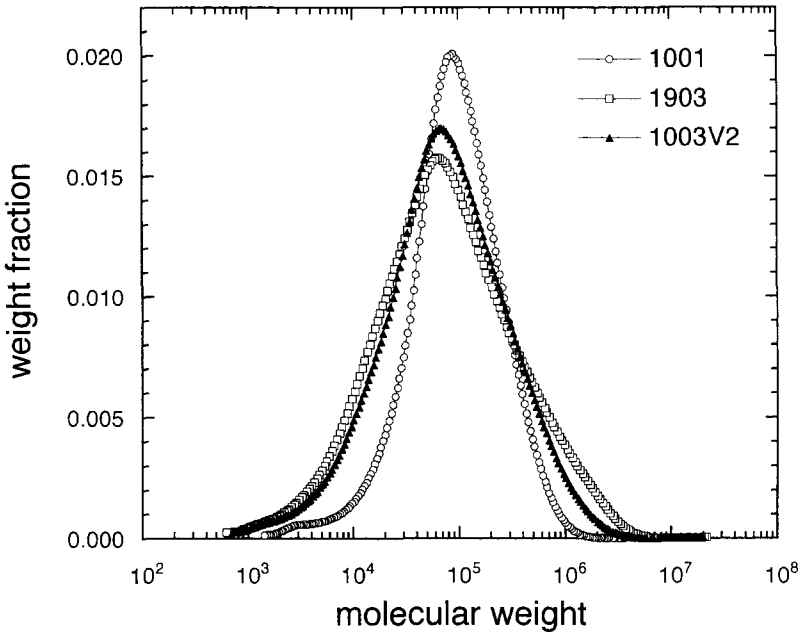

Figure 2 Real molecular weight distribution determined by s.e.c.–MALLS

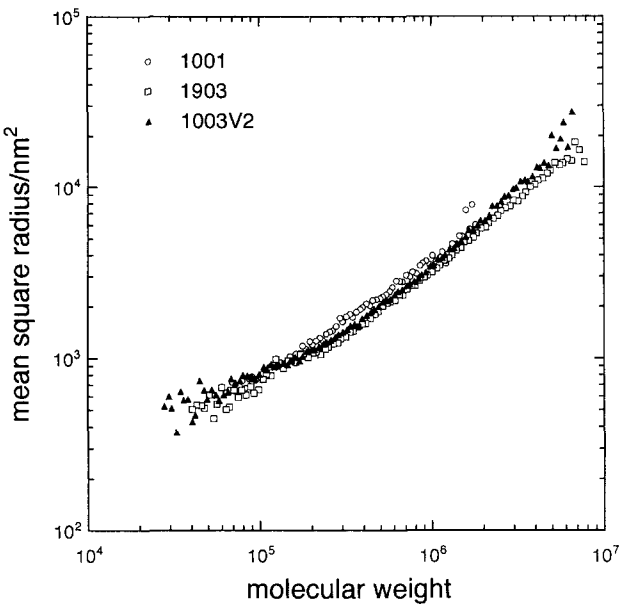

Figure 3 Mean square radius as a function of molecular weight

of polymer. In the s.e.c–MALLS experiments, smooth and monomodal chromatograms have been obtained for each samples by r.i. and MALLS detectors. Typical chromatograms are illustrated in *Figure 1*. It contains light scattering chromatograms of various scattering angles by the MALLS detector and a conventional concentration chromatogram by the r.i. detector. From these chromatograms, real molecular weight distribution has been directly determined. *Figure 2* shows molecular weight distribution of Bionolle polymers. The values of number-average, weight-average and z-average molecular weight (M_n, M_w and M_z, respectively), and the ratios of M_w to M_n and of M_z to M_w (M_w/M_n and M_z/M_w, respectively), which characterize molecular weight distribution, are listed in *Table 1*. Grade 1001 has relatively narrow molecular weight distribution as expected from the small swell ratio. Compared with the case of grade 1001, the broad molecular weight distribution might contribute to relatively large values of swell ratio for grades 1903 and 1003V2.

Though grade 1903 shows a very large value of swell ratio and the most excellent processing performance, its molecular weight distribution does not differ very much from that of grade 1003V2. One of the other factors contributing to viscoelastic properties of polymer is long chain branching. Its effect appears dramatically in melt elasticity such as swell ratio, which is related to the capability for extrusion coating and extrusion foaming. Meanwhile, long chain branching causes a decrease of the molecular size in solution at constant molecular weight. By s.e.c.–MALLS, mean square radius is determined simultaneously with molecular weight for each s.e.c. fraction, i.e. the molecular size as a function of molecular weight is obtained instantly.

Figure 3 shows the relationship between mean square radius and molecular weight for the Bionolle polymers. Comparing at the same molecular weight, the values of mean square radius for each sample are different; the value for grade 1001 is the largest, and the value for grade 1903 is the least. This fact indicates that these samples have different branched structures. According to the manufacturing method, mentioned above, while grade 1001 is a linear polymer, grades 1903 and 1003V2 may have some long chain branched structures.

Branching ratio (g_m) can be defined as the ratio of mean square radius of branched polymer to that of linear polymer with the same molecular weight. From the relations between mean square radius and molecular weight, g_m as a function of molecular weight has been evaluated for grades 1903 and 1003V2, and the results are illustrated in *Figure 4*. In the molecular weight range between 10^5 and 10^6, where g_m is evaluated quite reasonably in this study, g_m shows almost constant values, 0.82 for grade 1903 and 0.88 for grade 1003V2. Kurata and Fukatsu have calculated branching ratio for

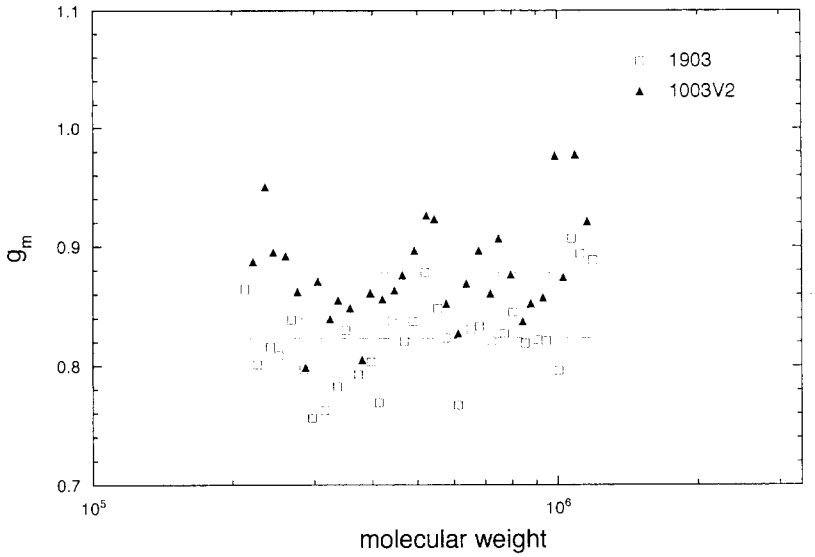

Figure 4 Branching ratio as a function of molecular weight for grades 1903 and 1003V2

various branched structures[6]. In the cases of grades 1903 and 1003V2, it seems that their calculation for random distribution of random branching is suitable. The branching ratio of 0.82 for grade 1903 is almost the same as the calculated value of 0.829 for two branches per molecule, and 0.88 for grade 1003V2 is close to the value of 0.900 for one branch per molecule. These comparisons suggest that grades 1903 and 1003V2 might have an H shape and a three-armed star shape on average, respectively.

Conclusions

By means of s.e.c.–MALLS, actual molecular weight distribution and mean square radius as a function of molecular weight have been evaluated simultaneously for some grades of Bionolle. For grades 1903 and 1003V2, the broad molecular weight distribution accords with larger values of swell ratio than that of grade 1001. From mean square radius as a function of molecular weight, branching ratio has been determined. Compared with the calculated values of branching ratio for random distribution of random branching, it is suggested that grade 1903 has an H shape structure with two long chain branches, and grade 1003V2 has a three-armed star structure with one long chain branch on average. It is concluded that these molecular structures contribute to melt elasticity and the capability for various polymer forming processes of the Bionolle polymers.

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