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Notes

Molecular Weight Determination of Fluorocarbon End-Capped Polyester Ultrathin Films by X-ray Photoelectron Spectroscopy

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Introduction

Investigations of the surface structures and surface properties of polymeric systems have been extensively done, both experimentally[1−5] and theoretically.[6,7] One goal of this work to design highly functionalized surfaces by chemical and physical surface modifications such as plasma treatment,[8] blending,[3−5] copolymerization,[9] synthesis of end functional dendrimers,[10,11] and so on since the structure and properties of materials at the surface are fairly different from that in the bulk. Electron spectroscopy for chemical analysis (ESCA), also called X-ray photoelectron spectroscopy (XPS), has been one of the most popular spectroscopic techniques available for the surface analysis of polymers because it provides elemental and chemical information about the material surface; quantitative information from chemical shifts allows the identification of surface functionality in a polymer, quantitative analysis of the surface allows the determination of elemental and functional-group concentrations, and angle-dependent measurements allow this information to be determined for different sampling depths.[12] The relationship between sampling depth and kinetic energy of emitted photoelectrons at the 90° takeoff angle can be described by various empirical equations; a typical one for organic materials was established by Seah and Dench[13]

$$\lambda = 490/E^2 + 1.1E^{1/2} \tag{1}$$

where λ is the inelastic mean free path (in angstroms) and E is the kinetic energy of the emitted photoelectrons (in electronvolts). λ can also be calculated using the modified Bethe equation[14]

$$\lambda = E/\{{E_p}^2[\beta \ln(\gamma E) - (C/E) + (D/E^2)]\} \tag{2}$$

where

$$E_p = 28.8(N_v \rho/M)^{1/2} \tag{3}$$

E_p is defined as the free-electron plasmon energy, calculated from N_v is the number of valence electrons per atom or molecule, ρ is the density (in g/cm^3), and M is the atomic or molecular weight. In eq 2, β, γ, C, and D are adjustable parameters.

In ESCA analysis, the sampling depth (d) is generally defined by

$$d = 3\lambda \sin\theta \tag{4}$$

where θ is the emission angle of the photoelectron. Under conventional conditions of an achromatic Mg Kα X-ray source, the magnitude of d for C 1s ranges from 2.7 to 10.3 nm, corresponding to takeoff angles of 15° and 90°, respectively.[12]

Polymeric films with thicknesses less than the maximum ESCA detection depth can be considered as a two-dimensional ultrathin film (2D film). Under these conditions, it is expected that the ESCA measurement of a 2D polymeric material with unique functional end groups might give its bulk composition. Even in an ultrathin film, segregation of a lower surface free energy component may occur at the topmost interface, and this may interfere with the determination of composition, if attenuation effects magnify the relative contribution of the surface segregation fraction. The purpose of present study is to evaluate the number-average molecular weight (M_n) of polymers having one functional end group on the basis of the angle-dependent ESCA. This is an adaptation of a sample method used with NMR.[15]

In general, techniques more commonly used for determining absolute molecular weights of polymers include light scattering, ultracentrifugation, and colligative properties.[15] Although the measurement of solution viscosities has been the most convenient method to determine molecular weights in the past, gel permeation chromatography (GPC or size exclusion chromatography (SEC)) is now becoming the most widely used method of determining molecular weight and also to have indication of the MWD.[15] However, as with intrinsic viscosities, this is a relative method,[16] and the molecular weights obtained may be in error because the result is dependent on the conditions used and the calibration method. In this paper, we report the M_n of fluorocarbon end-capped poly(lactide)s by means of angle-dependent ESCA, and it is compared to that measured by nuclear magnetic resonance (NMR) spectroscopy and SEC.

Experimental Section

Fluorocarbon mono end-capped poly(lactide)s (F-PLA) with different lengths of fluorocarbon, $CF_3(CF_2)_6CH_2$ and $CF_3(CF_2)_9CH_2CH_2$, were synthesized by ring-open polymerization of l-lactide (L-LA) or DL-lactide (DL-LA) by stannous octoate as a catalyst in the presence of fluorocarbon alcohol, pentadeca-

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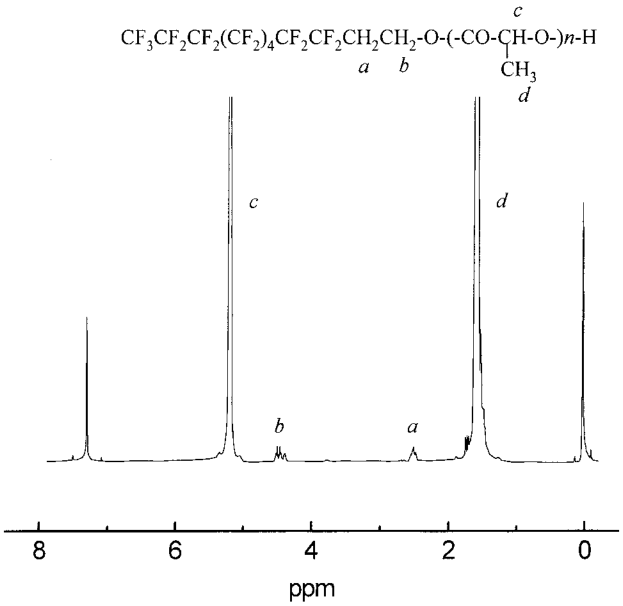

Figure 1. ^{1}H NMR spectrum of F10C2-L-PLA4 in $CDCl_3$.

fluoro-1-octanol (F*7*C*1*-OH; the italic digits give the carbon numbers of CF and CH groups, respectively) or 2-(perfluorodecyl)ethanol (i.e., F10C2-OH). The details of synthesis and characterization of F-PLA are discussed elsewhere.[17] ^{1}H NMR spectra were recorded on INOVA-500 (500 MHz) spectrometer using deuterated chloroform as a solvent. SEC analysis were carried out with a Knauer chromatography system equipped with a refractive index detector Erma ERC-7512 and a PLgel 5 mm MIXED-C column (300 × 7.5 mm) in a thermostat at 30 °C. Sample elution was conducted with chloroform with 1.0 mL/min flow rate. Calibration was performed by using monodisperse polystyrene standards.

The chemical compositions of the 2D films were obtained using a Perkin-Elmer Physical Electronic model 5300 ESCA. ESCA measurements were performed with Mg Kα X-ray source at 15 kV and 20 mA at takeoff angles of 30°, 45°, and 90°, which led to the sampling depths of the C 1s region of 5, 7, and 10.3 nm, respectively. When exposed to X-ray radiation, fluoropolymers are known to defluorinate. To minimize this effect, shorter exposure times (typically a total of 4 min) were determined from the relationship between exposure time and atomic ratio for poly(vinylidene fluoride) (PVDF) as a standard material. No defluorination of PVDF during this period was detected within the 95% confidence level, and this was set as the appropriate exposure time which could be tolerated. From here, we decided to use a separate sample for each measurement. All C 1s spectra were referenced to the neutral carbon of PLA at 285 eV, to correct charging effects. In the curve fitting, a Shirley type nonlinear background subtraction was used,[18] and the C 1s peaks were fitted using a least-squares routine assuming a Gaussian/Lorentzian (90/10) sum function. The 2D films were prepared by a spin-coating method (Photo Resist Spinner, Headway Research Inc.) using chloroform as a solvent on a clean silicon wafer. The thickness of films was controlled by changing the concentration of solution and the spin revolution. The film thickness was estimated from angle-dependent ESCA data using the absence of the substrate signal.

Table 1. M_n **of Fluorocarbon End-Capped Polyesters Measured by Different Instruments**

	M_n			
sample code	ESCA	^{1}H NMR	SEC	SEC
F10C2-L-PLA4	3710 ± 300	3810	14000[a]	5100[b]
F10C2-L-PLA11	10520 ± 1500	11730	29000[a]	11500[b]
F7C1-L-PLA	7350 ± 800	7570	24000[a]	9300[b]
F7C1-DL-PLA	4260 ± 700	5240	19000[a]	8800[b]

[a] Calculated from direct PS calibration only. [b] Calculated from universal calibration using the following *a* and *K* values: PS, $a = 0.794$ and $K = 0.49 \times 10^{-4}$ dL/g;[22] L-PLA, $a = 0.73$ and $K = 5.45 \times 10^{-4}$ dL/g;[23] DL-PLA, $a = 0.77$ and $K = 2.21 \times 10^{-4}$ dL/g.[23]

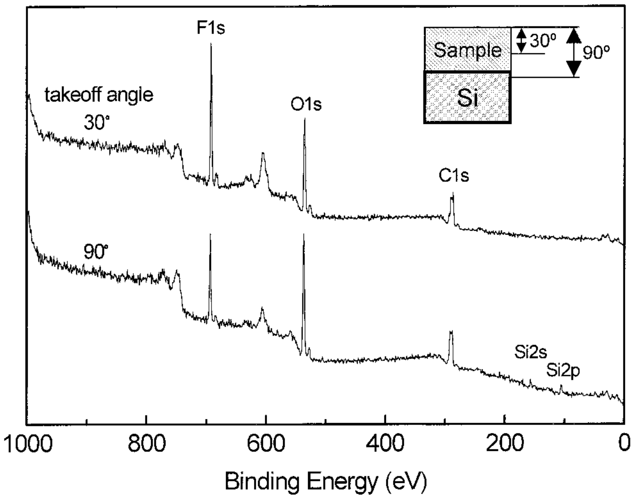

Figure 2. ESCA survey spectra of F10C2-L-PLA4 2D film taken at 30° (A) and 90° (B) takeoff angles. Inset illustrates the ESCA sampling depth of 2D films at different takeoff angles.

Results and Discussion

It is generally accepted that the ring-opening polymerization of lactide or glycolide can be initiated by alcohol. In this way, low or high molecular weight alcohols have been used to synthesize star-shaped polymers,[19] block copolymers,[20] and linear polymers with a specific end groups.[21] According to this method, the fluorocarbon mono-end-capped poly(lactide)s were synthesized by ring-open polymerization using F10C2-OH or F7C1-OH as functional initiator and stannous octoate as a catalyst. As an example, in the ^{1}H NMR spectrum of F10C2-*l*-PLA4, four signals are shown as assigned in Figure 1. The molecular weight of the F-polymers was calculated by the area ratio of peak *a* and peak *c* (see Table 1).

Angle-dependent ESCA gives quantitative information as a function of sampling depth, and this is very useful in understanding the phase or compositional separation of microstructures near an air surface.[24] Figure 2 shows ESCA survey spectra of F10C2-*l*-PLA ultrathin film on silicon wafer taken at 30° and 90° takeoff angles. At the 30° takeoff angle, signals from three elements (C, O, and F) of the sample are shown. This result indicates that the sample is wholly covered on the silicon wafer substrate. An AFM topographic image showed the homogeneous sample surface with roughness of ca. ± 1 nm. However, two small peaks in the lower binding energy region were newly observed in the survey spectrum at a takeoff angle of 90°. These peaks correspond to Si 2p and Si 2s of the silicon wafer as a substrate. From the ESCA sampling depth as a function of the takeoff angle, the thickness of the film (2D film) is between 5.6 and 11.2 nm, corresponding to sampling depths of Si 2p at 30° and 90° takeoff angles, respectively. Therefore, the spectrum taken at the 90° takeoff angle reflects the contribution of both whole sample and some of the substrate.

If the atomic components of the sample and the substrate are distinct from each other, we can get the bulk composition of the sample from the spectrum at a

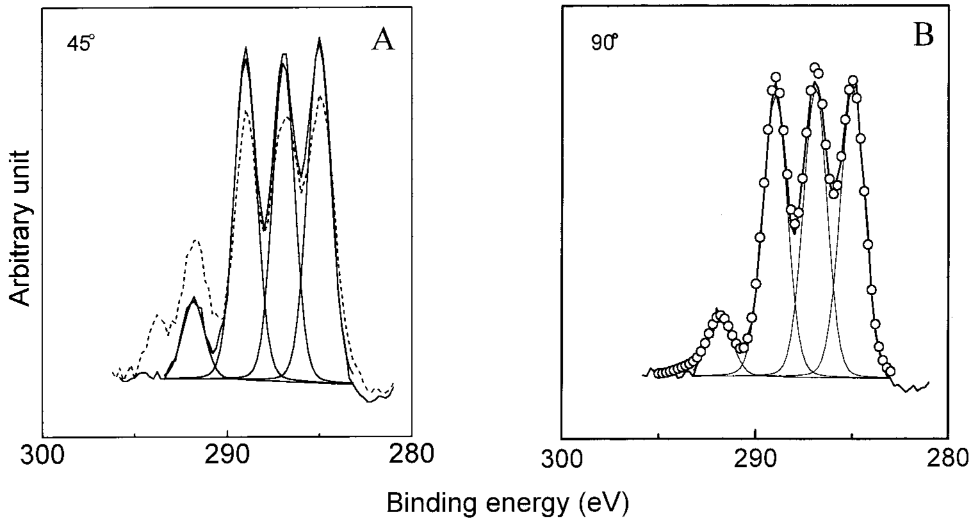

Figure 3. C 1s regions of F10C2-L-PLA4 ultrathin (solid line) and thick (dotted line) films taken at the 45° takeoff angle (A) and F10C2-L-PLA4 2D (solid line) film taken at the 90° takeoff angle (B). The open circles in Figure (B) represent the theoretically calculated C 1s peak of F10C2-L-PLA4.

takeoff angle of 90°. High-resolution C 1s spectra of F10C2-L-PLA ultrathin (2D) and thick films measured at the 45° takeoff angle are shown in Figure 3A. According to the polymer structure, the peak can be curve resolved into five components, with 285, 286.9, 289, 291.8, and 294.4 eV, corresponding to $-\mathrm{C}-C\mathrm{H}_3$, $-C-\mathrm{O}-$, $-C(=\mathrm{O})-\mathrm{O}-$, $-C\mathrm{F}_2-$, and $C\mathrm{F}_3$, respectively. This comparison clearly shows that the fluorocarbon concentration of the thick film is higher than that of the 2D ultrathin film. This discrepancy can be explained by considering that the conformational entropy of an individual chain in a constrained thin region is remarkably reduced in comparison to that of a thick film due to the fast evaporation of solvent molecules.[25] Thus, it is reasonable that polymer chains in the 2D film are almost stretched along the parallel direction, as expected by others.[26]

Since the ESCA photoemission intensity is attenuated exponentially with depth, the atoms in the upper surface region yield a higher contribution to the signal intensity than the atoms below the surface. To evaluate whether the surface structure of the 2D film shown in Figure 3A could attributed to the surface segregation of fluorocarbon groups or whether the film lacks such preferential orientation, the 90° takeoff angle was applied, as shown in Figure 3B (solid line). Figure 3B also shows the comparison of the theoretically calculated C 1s peak of F10C2-L-PLA4 on the basis of its bulk composition (open circles). There are no significant differences in both results from different takeoff angles (signal attenuation effect) and the theoretical calculation.

Thus, we conclude that under the rapid formation condition of spin-casting an ultrathin film, preferential orientation of an fluorocarbon end groups does not occur. This is unlike thick films when preferential end group segregation occurs.

To minimize the effect of any surface contamination, the peaks at takeoff angle of 90° were used for calculations of M_n. Since the ESCA spectrum of the cleaned silicon wafer gives only one peak at 285 eV in the C 1s region, corresponding to the neutral carbon and its intensity is relatively smaller than those of Si 2p and O 1s, it seems reasonable to use the $\mathrm{CF_2/CO}$ or $\mathrm{CF_2/COO}$ ratio in the C 1s region for the quantitative evaluation of the pure sample composition. To calculate M_n, the $\mathrm{CF_2/CO}$ ratio was used to avoid the contribution of silicon substrate in the C 1s region. Then, the M_n of F10C2-PLA was calculated by using eqs 5 and 6,

$$\frac{\mathrm{I}C\text{-}\mathrm{F}_2}{\mathrm{I}C\text{-}\mathrm{O}} = \frac{9}{1+n} \tag{5}$$

$$M_n = 563 + 72.1n \tag{6}$$

where Ii is the integrated intensity of a core−electron photoemission spectrum and n is the ratio of lactide unit to fluorocarbon unit; 563 and 72.1 are the molecular weights for F10C2-O- and lactide monomer unit, respectively.

The SEC analysis can give useful information about M_n, the molecular weight distribution, and the presence of residual monomers; in the present case, unimodal curves were found, and no significant fractions of low molecular products was detected in the samples. Also, we tried to calculate the M_n using the Mark−Houwink values for poly(lactide)[23] measured at the same conditions of SEC because the Mark−Houwink parameters for the polymers studied here are not available. The obtained M_n values are similar to those found from NMR and ESCA analysis. The difference may be partly attributed by the presence of fluorine segments, which can modify the hydrodynamic properties of the overall polymer and therefore affect the accuracy of M_n from SEC calibrated by polystyrene standards.

Table 1 summarizes the average number molecular weights of F-PLA measured by different instruments, NMR, ESCA, and SEC. The M_n determined by ESCA measurement is equivalent to that from NMR. However, the M_n measured by SEC, using a direct PS calibration method, is much higher than those of NMR and ESCA. In conclusion, the M_n of fluorocarbon end-capped poly(lactide)s has been evaluated on the basis of angle-dependent ESCA. This method might be more useful to measure the M_n of copolymers if the composition of each unit in the copolymer is not too low and each unit has a unique atom.

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