Polymer Journal, Vol. 3, No. 2, pp 242—243 (1972)

SHORT COMMUNICATION

ESCA Spectra of Poly(γ-benzyl-L-glutamate)

Riichirô Chûjô, Kazuo Sato, and Atsuo Nishioka

Department of Polymer Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan.

(Received July 9, 1971)

KEY WORDS Poly(γ-benzyl-L-glutamate) / Helix—Coil Transformation / Lifson—Roig Theory / ESCA /

There have been reported many theoretical and experimental studies on helix—random coil transformation in polypeptides. However, some kind of gap lies between theoretical and experimental studies, namely, it is convenient theoretically to consider that the phase space is composed of a coil domain, a helix domain, a and third domain,[1] while the third one has not been detected experimentally, as yet, due to the lack of appropriate experimental techniques. The third domain is thought to be a local conformation of the repeating unit in this region corresponding to helical one, but the helical conformation cannot be formed due to the lack of interaction with the other repeating units (according to the notation of Lifson and Roig,[1] the partition function contributed from this domain being v). In order to detect this domain experimentally, we must use a technique sensitive to the local character of interaction in the sample used. A recently developed technique, ESCA (electron spectroscopy for chemical analysis),[2] is most appropriate at this stage. The purpose of this short communication is to report the quantitative characterization of the third domain with the aid of ESCA.

The sample used was poly(γ-benzyl-L-glutamate) ($M_v=1.47\times10^5$) prepared by the Nakajima laboratory at Kyoto University and supplied by courtesy of Professor A. Nakajima. Sample no. 1 was a 5-% solution of the polymer in chloroform. Sample no. 2 was a 5-% solution of the polymer in the mixed solvent of trifluoroacetic acid and chloroform (50/50). Both samples were prepared at 20°C, liberated from the solvent by the freeze-dry method, and kept at that state for a few days. Spectra were measured by an IEE Spectrometer manufactured by Varian Associates. In order to avoid the overlap of the peaks assigned to the samples with those from residual solvents, the spectra of photoelectrons emitted from 1s orbit in nitrogen were measured.

The spectrum of sample no. 1 is reproduced in Figure 1. Each of dotted point corresponds to multiscan averaged datum after a scanning of 100 times and the continuous curve corresponds to the spectrum obtained by the smoothing of the data of succeeding three representative points. There is a sharp peak at 400.5 eV. This peak

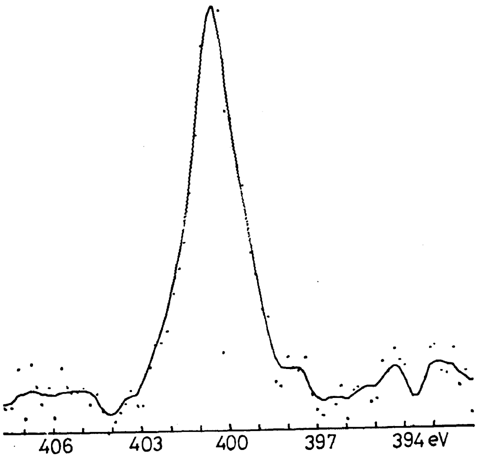

Figure 1. Photoelectron spectrum emitted from 1s orbit in nitrogen of poly(γ-benzyl-L-glutamate). Sample was frozen-dry from 5-% solution in chloroform.

can be assigned to the nitrogen atoms hydrogen-bonded with a carbonyl group, because chloroform is a helix solvent for poly(γ-benzyl-L-glutamate). On the other hand, the spectrum of Sample no. 2 is split into two peaks as shown in Figure 2. The dotted points and the continuous curve are obtained in a similar fashion to those in Figure 1. The chemical shifts of these two peaks are 399.8 and 400.3 eV's, respectively. The splitting between these two peaks is rather small, but this is confirmed both qualitatively and quantitatively by the repetition of measurements. The remaining minor peaks will be considered after the reliability of the equipment is verified in future. The mixed solvent used for this sample is a coil one, so that above splitting is due to the difference of the binding energies between the coil and the third domains above mentioned. From the comparison with the value of the chemical shift for sample 1, the values, 399.8 and 400.3 eV's can be assigned to the coil and the third domains, repectively. The intensities of these two peaks are 36 and 64-%, respectively. It can be concluded that ESCA served for the quantitative characterization of the third region in polypeptide, and that the third region occupies 64-% of phase space for poly(γ-benzyl-L-glutamate) in a coil solvent.

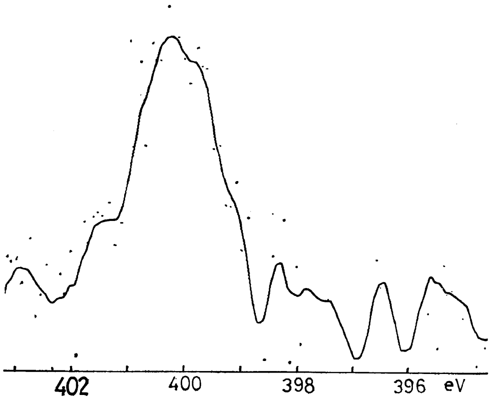

Figure 2. Photoelectron spectrum emitted from 1*s* orbit in nitrogen of poly(γ-benzyl-L-glutamate). Sample was frozen-dry from 5-% solution in the mixed solvent of trifluoroacetic acid and chloroform (50/50).

Acknowledgments. The authors would like to express their sincere thanks to Professor A. Nakajima at Kyoto University for his courtesy in supplying the sample. Their thanks are also due to Messrs. M. Yamanouchi and K. Kushida at Nippon Electric Varian Co., Ltd. for their kind arrangements concerning measurements with ESCA.

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