# Morphological Study by TEM on Electrospun Nanofibers of polydioxanone

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## Introduction

Polydioxanone (PPDX) is a polyester-ether, as illustrated in the following formula: $[-CH_2-CH_2-O-CH_2-CO-O-]_n$. Recently, our research group reported the detailed analysis for crystal structure and conformation of PPDX[1]. PPDX is widely used in the medical field since PPDX has an excellent physical characteristic and a preferable moderate biodegradation rate.

In general, in case of polyester fiber, the fibrous structure will greatly influence the degradation behavior. In order to control biodegradability of the fiber, it is necessary to understand the relationship between the morphology and degradation mechanism. In our previous work, a stacked-lamellar-like structure has been visualized in melt-spun PPDX fibers by permanganic etching and X-ray analysis. Now, we are really interested in the formation mechanism of such crystalline lamellae.

The major object of this study is to know the morphology of PPDX fiber crystallized under the flow field. Therefore, PPDX nanofibers were prepared by electrospinning method[2,3] and examined by transmission electron microscopy (TEM).

## Experimental

**Materials.** PPDX pellet (weight-average molecular weight = 369,000 and polydispersity (DPI) =3.6) were supplied by Alfresa Phama corporation.

**Electrospinning.** The 3.0 wt% solution of PPDX in 1,1,1,3,3,3 hexafluoro-2-propanol was prepared. The electrospinning apparatus was carried out with an esprayer ES-1000 (fuence Co., Ltd.). The PPDX solutions were loaded into a glass syringe with a 21 gauge needle made of stainless steel. The needle was connected to a high-voltage supply that is capable of generating DC voltages up to 24 kV. The solution was continuously supplied using a syringe pump at a rate of 0.3 and 1.5 mL/h. A voltage of 20 kV was applied for electrospinning. The distance between the needle tip and the collector was 10 cm. In order to align and collect nanofibers parallel to each other, we used specially designed a collector consisting of two conductive substrates, according to the idea proposed by Li et al[3].

**Treatment of Electronspun nanofibers.** Electrospun nanofibers were drawn to 2.0 times and heat treated for 12h in 80 ℃. For TEM observation, the electrospun nanofibers, which had been drawn and heat-treated, were mounted on carbon-coated copper grids.

**Transmission Electron Microscopy.** Morphological observation and selected-area electron diffraction (SAED) of resulting specimens were performed at room temperature with a transmission electron microscope, JEOL JEM-200CS, operated at an accelerating voltage of 200 kV. All images and SAED patterns were recorded on photographic films (Mitsubishi MEM) which were then developed with Mitsubishi Gekkol (full strength) at 20 ℃ for 5 min.

## Results and Discussion

Fig.1 shows optical micrograph of electrospun nanofiber collected by homemade collector under cross-polarized optical microscopy. This image clearly indicated that the electrospun nanofibers were parallely aligned. By polarized light microscopy, strong birefringence was recognized for electrospun nanofibers. Therefore this result indicates that the polymer chains are preferentially oriented along the fiber axis.

Fig.2 is SAED patterns of electrospun PPDX nanofiber prepared from 3.0 wt% solution. In the SAED pattern of as-electrospun nanofibers (Fig.2 (a)), crystalline peak is hardly seen. That is to say, the randomly deposited nanofibers on a collector did not crystallize. The SAED pattern of aligned nanofibers (Fig(b)), however, exhibits crystalline reflections. It is suggested that parallelly aligned nanofibers were partially crystallized when they were deposited on our collector. After drawing and/or heat treatment, the SAED patterns of aligned nanofibers show a well-developed fiber pattern, and in the patterns we can observe crystalline reflections up to third layer line. These patterns are nearly equal to the wide-angle X-ray diffraction patterns of melt-spun fibers.

## Conclusions

PPDX nanofibers for TEM observation can be produced. To collect parallelly aligned nanofibers can crystallize them partially. The SAED pattern of nanofibers drawn and/or heat-treated shows a well-developed fiber pattern.

## References

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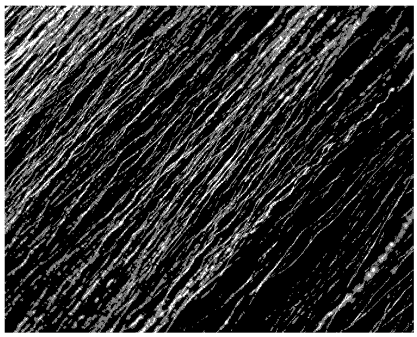

Fig.1 Optical micrograph of electrospun fibers under cross-polarized optical microscopy.

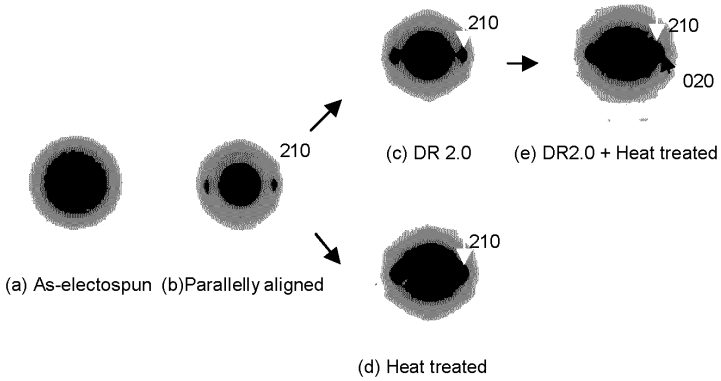


Fig.2 SAED patterns of electrospun PPDX prepared from 3.0 wt% solution): (a) as-spun, (b) parallelly aligned nanofibers, (c) parallelly aligned nanofibers drawn to 2.0 times, (d) heat-treated under 80 ℃ for 17h and (e) drawn to 2.0 times and heat-treated under 80 ℃ for 17 h.