



# Effect of phase morphology on water diffusion in phosphorus-containing thermotropic liquid crystal copolyester film



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## ABSTRACT

In this paper, effect of phase morphology on water diffusion in phosphorus-containing aromatic liquid crystalline copolyester (P-TLCP) named as poly(-hydroxybenzate-co-DOPO-benzenediol dihydrodiphenyl ether terephthalate) (PHDDT) was investigated by two-dimensional correlation infrared (2DIR) spectroscopy, in order to understand well the relationship between structure and properties of P-TLCP. The phase morphologies of the PHDDT films were observed by polarized light microscope. The experimental results showed that the clear nematic texture, which was observed for PHDDT film treated at 250 °C for 3 min under a nitrogen atmosphere. However, lots of bright spots were observed for untreated PHDDT film due to weak crystallization of PHDDT molecules. Moreover, the density of the untreated PHDDT film ( $1.1631 \pm 0.0257 \text{ g/cm}^{-3}$ ) was lower than that of the treated one ( $1.2969 \pm 0.0134 \text{ g/cm}^{-3}$ ), indicating that the arrangement of the molecules in treated PHDDT film was compact in comparison with that in untreated one. Therefore, the average diffusion coefficient of water in treated PHDDT film was lower than that in untreated one. The mechanisms of water diffusion into PHDDT films with different phase morphologies can be obtained through 2DIR analysis in OH stretching and bending bands. It was found that water diffused into the treated PHDDT film by forming moderate hydrogen bonds prior to forming strong and weak hydrogen bonds, while diffused into the untreated one by forming strong and weak hydrogen bonds prior to forming moderate hydrogen bonds. It was also found that the spectral intensity of P=O varied prior to that of C=O during water diffusion into untreated PHDDT film, which was reversed for treated PHDDT film.

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## 1. Introduction

Thermotropic liquid crystalline polymers (TLCPs) have good thermal stability, outstanding chemical resistance [1–4], high strength, high modulus and excellent mechanical properties [5,6], as well as low linear viscosity in liquid crystalline state [7,8]. Therefore, it becomes attractive high performance engineering materials for variety of industrial applications [9,10]. However, in order to obtain good safety during the applications of TLCP, it is necessary to require high flame retardancy for TLCP. To solve this problem, the elemental phosphorus as an efficient flame retardant is introduced into the molecular structure of TLCP. Therefore, a phosphorus-containing aromatic TLCP (P-TLCP) is used as a macromolecular halogen-free flame retardant, whereas P-TLCP can also keep good mechanical properties of TLCPs. Wang et al. have successfully synthesized a series of P-TLCP

with high flame retardancy (limited oxygen index, 70%) [11–13], which were used to prepare in situ composite with poly(ethylene-terephthalate) (PET) and polycarbonate (PC). It had been found that, except for good flame retardancy, the composites also obtained a good mechanical property by in situ self-reinforcement with the P-TLCP fibrils formed in PET and PC matrix during processing [14]. However, when TLCP is in humid environment during the storage and processing, it will absorb water molecule so that the degradation of TLCP occurs during processing. As a result, there are negative effects on properties of the product, such as decreasing of mechanical properties, appearing bright stripes on the surface, and changing the internal stress of the products [15,16]. In addition, it is well known that the morphological structure of polymer strongly determined its' property [17–20]. For TLCP, the liquid crystalline phase transition can take place when TLCP is heated and reached to mesophase transition temperature, and this mesophase structure, to some degree, will also determine the properties of TLCP. Hence, to understand well the relationship between structure and properties for TLCP, it is necessary to investigate the interactions between TLCPs with different phase morphologies and water diffusion at the molecular level.

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Various experimental methods used to investigate water diffusion into polymers, include gravimetric sorption [21], laser interferometry [22], quartz crystal micro-gravimetry [23], nuclear magnetic resonance spectroscopy (NMR) [24], and Fourier transform infra red spectroscopy (FTIR) [25–30]. Among the methods of measuring water diffusion process in polymer matrix, ATR-FTIR is one of the most effective ways to detect the whole diffusion process in real time [31]. The in situ time-resolved ATR-FTIR can measure not only the water diffusion coefficient [25] but also the mechanism of water molecular interaction between water and polymer [26,32]. Sammon [33,34] investigated the water diffusion process and found four different states of water OH stretching vibration in polymer matrices such as PET and Poly (vinyl chloride) (PVC), by using ATR-FTIR spectroscopy. In recent years, generalized two-dimensional (2D) correlation FTIR spectroscopy proposed by Noda has been developed to analyze various kinds of spectral data, which can provide the information on different molecular functionalities as well as the relative sequence order of the spectral intensity changes under the course of the perturbation, and also reveal molecular dynamics in a polymer matrix [35]. Through this method, Wu and his colleagues [36] proposed the water diffusion process in poly(3-caprolactone) (PCL) polymer matrix as: water molecules diffused firstly into the free voids of PCL matrix or were molecularly dispersed into the matrix and then formed the hydrogen bonds with hydrophilic C=O group of PCL forming the bound water in polymer matrix. By using 2D correlation analysis on ATR-FTIR spectra, effects of chemical composition or crystallinity on water diffusion in other polymers such as poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx), aromatic polyamide, polypropylene, and epoxy resins, also have been studied [37–40]. Therefore, ATR-FTIR should be used as a good method to investigate effect of phase morphology on water diffusion in P-TLCP film.

In this work, effect of phase morphology on water diffusion in the phosphorus-containing aromatic TLCP (P-TLCP) film is investigated by time-resolved ATR-FTIR. Through the 2D correlation analysis, the specific water diffusion sequence will be obtained, and the dynamics of water diffusion in P-TLCPs with different phase morphologies will be also discussed. Furthermore, the average diffusion coefficients will be obtained during the water diffusion in P-TLCP films with different phase morphologies through the non-linear curve fitting.

## 2. Experimental

### 2.1. Materials

Terephthalic acid (TPA) was supplied by Zhenghao Advanced Fiber Materials (Jinan, China). 4, 4'-diacetyldiphenyl ether (DOP) was supplied by Suzhou New District BEC Fine Chemicals (Suzhou, China). 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was kindly provided by Weili Flame Retardant Chemicals, Chengdu, China. *p*-hydroxybenzoic acid (*p*-HBA) and *p*-acetoxybenzoic acid (*p*-ABA) were purchased from Wulian Chemical Company, Wulian, China. Other chemical agents such as 2-ethoxyethanol, zinc acetate (Zn(Ac)<sub>2</sub>), *p*-benzoquinone and acetic anhydride (Chengdu Chemical Reagent Plant, Chengdu, China) were also commercially available. All chemical agents were used without any further purification.

### 2.2. Monomer synthesis

According to a published procedure [41,42], 2-(6-oxid-6H-dibenz < c, e > < 1, 2 > oxaphosphorin6-yl)1,4-benzenediol (DOPO-HQ) was synthesized from DOPO and *p*-benzoquinone. 2-Ethoxyethanol was used as a reaction solvent. Acetylated DOPO-HQ (DOPO-AHQ) was prepared by the refluxing of DOPO-HQ with acetic anhydride for 13 h under a nitrogen atmosphere. The reaction mixture was poured into a large excess of distilled water. The pre-capitates that formed were filtered and washed with distilled water. The product DOPO-AHQ was re-crystallized from aqueous ethanol and then dried in vacuum oven at 70 °C for 24 h. The product yield of DOPO-AHQ was 91%, and the melting point was 102–104 °C. DAODP was prepared by a similar way of DOPO-AHQ.

### 2.3. Polymer synthesis

In this study, a phosphorus-containing aromatic liquid crystalline copolyester (P-TLCP) named as poly(-hydroxybenzate-co-DOPO-benzenediol dihydrodiphenyl ether terephthalate) (PHDDT, Fig. 1) was synthesized by melting transesterification from *p*-HBA, TPA, DOPO-AHQ, and DAODP at the overall molar ratio of 10:5:4:1. A three-neck flask, which was filled with *p*-HBA, TPA, DOPO-AHQ, and DAODP, was equipped with a mechanical stirrer, a nitrogen inlet and a distillation trap connected to a vacuum line. 0.3 wt% Zn(Ac)<sub>2</sub> was added as a catalyst for transesterification. The nitrogen should be introduced to blow out air in the flask before reaction and then put the flask in a salt bath preheated to 200 °C. The reactor was then heated step wise: 1 h to 260 °C, and held 1 h at 260 °C, 0.5 h to 280 °C and held 1 h at 280 °C. After these steps, a vacuum was applied, at the same time the reaction system should be heated to 300 °C in 0.5 h with a vacuum of about 80 Pa. At last, the temperature was kept at the 300 °C with a high vacuum of 60 Pa for 1 h. When the polymerization was completed, the flask was cooled to ambient temperature in the air under vacuum. The intrinsic viscosity of copolymer was measured by Ubbelohde capillary viscometer in a mixture solution of phenol-1,1,2,2-tetrachloroethane (50:50 w/w) at 30 °C at a concentration of 0.1 g/dL. The value of the intrinsic viscosity of copolymer was 0.49 g/dL. The detailed properties of PHDDT in this paper were described in the reference [13], where it was named as PHDDT20.

### 2.4. Samples preparation and morphological observation

PHDDT was dissolved in phenol/tetrachloromethane (volume ratio, 1:1) mixed solvent, and the concentration was 20 g/L. The solution was cast onto a glass plate in diameter of 60 mm in fume hood. After being left in the air at room temperature for 24 h, the glass plate was dried in a vacuum oven at 80 °C for 12 h to remove residual solvent and finally cooled slowly down to room temperature. The films were peeled off from the glass plate. The thickness of the sample films was measured by a Coatest-1000 nonferrous digital coating thickness gauge (Jinan SanQuan experiment instrument co., Shandong, China). The thickness of the P-TLCP film was ~20 μm. The untreated film of PHDDT was named as sample A, and the film of PHDDT (sample B) was treated in a temperature control instrument under a nitrogen atmosphere for 3 min at 250 °C, then the sample B was immersed in liquid

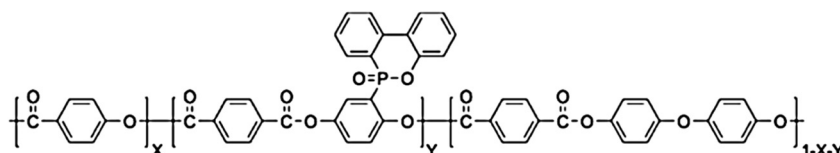


Fig. 1. Chemical structure of PHDDT, where X, Y, and 1-X-Y denoted the overall composition in molar ratio, which were not the block length.

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