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# ATR FTIR spectroscopic study on acceleration effect of additives on guest exchange process of Syndiotactic polystyrene complexes

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ABSTRACT

Syndiotactic polystyrene (sPS) forms co-crystal structures with a variety of chemical compounds. The guest exchange procedure is an effective way to prepare sPS co-crystals. The substitution is caused by exposing an sPS co-crystal film to a vapor, a liquid or a solution of the new guest molecule. In particular, the addition of an additive, such as chloroform, to the liquid of new guest molecule promotes the guest exchange process and makes bulky molecules easily incorporated into the crystalline region of sPS co-crystals. In order to obtain further information about the influence of additive as accelerant, the sorption and desorption processes of new and old guests during the guest exchange of sPS/chloroform ($CHCl_3$) co-crystal film were followed with ATR FTIR spectroscopy. A series of n-alkanes from n-hexane to n-decane and deuterated chloroform ($CDCl_3$) were employed as new guests and an accelerant additive. The apparent diffusion coefficients of the new and old guests were evaluated from the intensity changes of their IR bands. It has been shown that the addition of $CDCl_3$ promotes the guest exchange between the original guest ($CHCl_3$) and n-alkanes significantly and this effect becomes more pronounced as n-alkane chain-length increases. The diffusion of n-alkanes in atactic polystyrene was also studied for comparison, which suggested that the additive plays an important role at the stage of n-alkane uptake from the amorphous region to the crystallites.



## 1. Introduction

Syndiotactic polystyrene (sPS) has a unique feature that has not been found in other polymeric materials. It exhibits polymorphism; a variety of crystalline states appear depending on crystallization conditions and thermal history [1]. Furthermore, it forms molecular complexes with low mass compounds in gel and crystalline states [2,3]. The complexation of sPS attracts a wide range of interest since it has been demonstrated that sPS can incorporate a wide range of chemical compounds with different size, shape and property into its crystalline region, such as dye, fluorescent, photo-reactive, paramagnetic, optical active molecules, and so on [4–10]. Recently, it was also found that sPS can accept oligomeric compounds with molecular weight around 1000 [11]. Depending on the preparation conditions and the nature of guest molecules, sPS exhibits at least four kinds of co-crystalline structures consisting of sPS helices of $(T_2G_2)_2$ conformation: the monoclinic δ-clathrate [12,13] and intercalate co-crystals [14], the orthorhombic ε–clathrate co-crystal [15] and the triclinic δ-clathrate co-crystal [16].

The crystalline complex formation of sPS was originally carried out by solution-cast and solvent-induced crystallization. However, there are not many chemical compounds available as solvents for these methods. Guest exchange is another method to prepare sPS crystalline complexes [17–19]. The original guest is replaced with a new compound by exposing sPS films to a vapor or a liquid of the substitute.The guest exchange method has an advantage that enables sPS to form crystalline complexes even with chemical compounds that are difficult to incorporate into the crystalline region by the solution-cast and solvent-induced crystallization methods. Furthermore, the addition of an additive significantly promotes the guest exchange process of sPS complexes [20]. For example, the mixing of chloroform into the liquid of n-decane makes the uptake of n-decane into the sPS lattice proceed much faster. The additive-assisted guest exchange method has extended the range of chemical compounds available as guests. For example, bulky molecules such as TEMPO and 18-crown-6 as well as long-chain molecules such as polyethylene glycol oligomers have been incorporated into the crystalline region.

Although the high validity has been confirmed by many examples, the characteristics of the additive-assisted guest exchange

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have not been investigated in detail. For example, the influence of the additive on the guest exchange rate has not been estimated quantitatively. Furthermore, it is still unclear how the additive accelerates the guest exchange, though it is considered to act as a plasticizer.

In this study, we tried to evaluate concretely the acceleration of guest exchange due to an additive chloroform. For this purpose, we choose a series of n-alkanes from n-hexane to n-decane as new guests, because the influence of guest size can be evaluated by changing the chain length systematically [21–24]. By using a feature of ATR FTIR spectroscopy, specifically, the ability to monitor outgoing old and incoming new guests in-situ simultaneously, we followed the sorption and desorption of the two guests under the influence of the additive in order to study the changes in diffusion coefficients of the incoming and outgoing guests. Since it was difficult to evaluate diffusion coefficients in the amorphous and crystalline regions separately, we tried to obtain the apparent bulk diffusion coefficients for simple data analysis. In addition, the diffusion of n-alkanes in atactic polystyrene (aPS), a typical amorphous polymer, was also studied for comparison.

In this paper, we will report how the addition of chloroform changes the guest exchange behavior for a series of n-alkanes from n-hexane to n-decane. It will be shown that the influence of the additive appears more clearly as the size of the incoming guest increases and that the addition of a relatively small amount of the additive (less than 10 wt%) effectively accelerates the guest exchange of long n-alkanes. Based on the experimental results, we will discuss the role of the additive chloroform for the acceleration of the guest exchange process.

## 2. Experimental section

### 2.1. Samples

sPS was supplied by Idemitsu Petrochemical Co. Ltd. The weight-average molecular weight ($\overline{M}_w$) was 179 k and the polydispersity index ($\overline{M}_w/\overline{M}_n$) was 3.08. aPS with of 240 k, was purchased from Sigma–Aldrich Co. Chloroform ($CHCl_3$) of purity 99%, deuterated chloroform ($CDCl_3$) of isotope purity 99.8% and a series of *n*-alkanes (*n*-hexane of purity 96%, n-heptane of 99%, n-octane of 98%, n-nonane of 98% and *n*-decane of 98%) were purchased from Nacalai Tesque and used without further purification.

### 2.2. Measurements

Transmission and ATR FTIR spectra were taken with a JASCO FTIR-610 spectrometer equipped with an MCT and D-TGS detector at a resolution of 2 $cm^{-1}$. For ATR measurements, a homemade ATR device (Fig. 1) consisting of an internal reflection element (IRE) of KRS-5 prism (29.5 × 10 × 3 mm) with a bevel of 60° and a stainless cover that makes a liquid reservoir room to keep a mixture of new guest and additive over the sPS film on the prism. The incident angle of IR radiation was set at 60° and the penetration depth ($d_p$) around 1000 $cm^{-1}$ was 1.1 μm. The number of accumulation cycles was 8 in the first 10 min from the initiation of the guest exchange process and 32 from then onward.

### 2.3. Guest exchange experiments

In order to differentiate chloroform used as a guest and as an additive, a protonated chloroform and a deuterated one, $CHCl_3$ and $CDCl_3$, were employed, respectively. The starting film of sPS/$CHCl_3$ complex was prepared by casting a $CHCl_3$ solution of sPS (3 wt%) onto an IRE of KRS-5 and letting it stand at least for one hour at room temperatue. The thickness of the film and the concentration

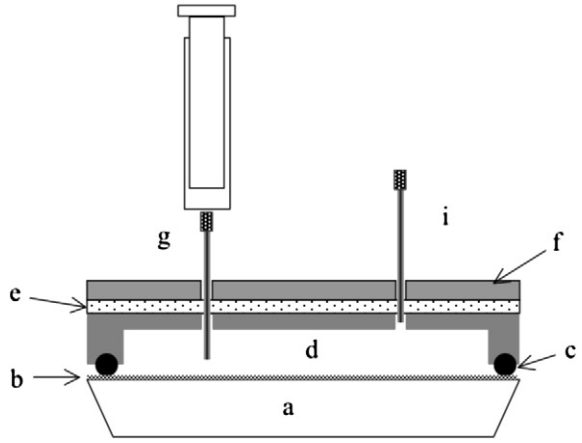


**Fig. 1.** Schematic representation of the ATR device used for guest exchange measurements; a: IRE, b: sPS film, c: o-ring, d: reservoir, e: rubber sheet, f: rubber cramp, g: syringe needle for new guest injection, and i: syringe needle as a gas vent. After the injection of a liquid into the reservoir, the two syringe needles are removed and the rubber sheet acts as a plug.

of $CHCl_3$ in it were about 12 μm and 7 wt%, respectively, which were determined by comparing the intensities of the phenyl band at 1601 $cm^{-1}$ and the chloroform band 1219 $cm^{-1}$ in the transmission FTIR spectrum with that of a free standing film of known thickness and concentration.

The guest exchange was initiated by injecting a mixture of new guest n-alkane and $CDCl_3$ into the liquid reservoir room of the ATR device. Just after the injection, n-alkane molecules started to penetrate into the film and exchange with the original guest chloroform. Since the evanescent electric field produced by total reflection of IR radiation does not practically reach the opposite film surface, n-alkane molecules in the reservoir does not contribute to the ATR spectrum. Only after n-alkane molecules come within the effective range of the evanescent field, they appear in the spectrum. Accordingly, the rate of intensity increase of the bands due to n-alkane reflects how fast the amount of n-alkane in the sPS film increases by guest exchange.

### 2.4. Data analysis

The theory developed by Fieldson and Barbari [25] and by Xu and Balik [26] for the analysis of diffusion of small molecules in a polymer film by using ATR-FTIR data was employed to evaluate the diffusibility of the old and new guests, as was in our previous study for the guest exchange and desorption processes in sPS [18].

Assuming that a chemical species is initially uniformly distributed in a polymer film of thickness *L*, that one face of the film is in close contact with the surface of the IRE and the other face is a free surface, and that the release of the chemical species to the outside takes place only at the free surface, the IR absorption intensity of the chemical species, $A_t$, has the following relation to its initial intensity $A_0$ when time *t* has passed since the inception of the release.

$$\frac{A_t}{A_0} = \frac{8\gamma}{\pi[1-\exp(-2\gamma L)]} \times \left[\frac{\exp\left(\frac{-D\pi^2 t}{4L^2}\right)\left(\frac{\pi}{2L}\exp(-2\gamma L)+2\gamma\right)}{4\gamma^2+\frac{\pi^2}{4L^2}}\right] \quad (1)$$

Here, *D* is the diffusion coefficient of the chemical species, and γ is a parameter to describe how the evanescent electric field in the