

## Research Article

# Direct Evidence of $\pi$ - $\pi$ Interactions in Transparent Organic-Inorganic Polymer Hybrids of Polystyrene and Silica Gel

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Polystyrene and silica gel polymer hybrids derived from polystyrene and phenyltrimethoxysilane via  $\pi$ - $\pi$  interactions were synthesized by a slight modification of the previous method. Spectroscopic evidence of the  $\pi$ - $\pi$  interaction is provided. The obtained polymer hybrids were optically transparent, and no phase separation was observed by scanning electron microscopy measurements. In the FT-IR spectrum of the resulting polymer hybrids, the absorption peaks corresponding to C-H wagging vibration shifted to a lower wavenumber range as the content of silica in the hybrids increased. A UV-vis spectrum of the polystyrene and silica gel polymer hybrids showed a shoulder peak at around 260 nm that shifted toward longer wavenumbers side as the content of silica increased. These results clearly indicate that  $\pi$ - $\pi$  interactions contribute to the formation of these transparent hybrids.

## 1. Introduction

Since the 1990s, many research studies have reported on polymer hybrids and polymer composites. Especially, organic-inorganic polymer hybrids have been developed as useful materials having excellent properties such as transparency, thermal stability, flexible mechanical properties, and others [1–4]. Transparent and homogeneous polymer hybrids can be obtained at the molecular level via the dispersion of an organic polymer and inorganic metal oxide matrix. Two main methods are widely known for preparing such homogeneous organic-inorganic polymer hybrids. One method involves covalent bonding between the organic and inorganic components through silane coupling groups on organic segments. The other method involves intermolecular interactions such as a hydrogen bonding interaction between an organic polymer and an inorganic metal oxide matrix. In particular, the latter is very simple and industrially useful because new materials can be obtained only by adding metal alkoxides into an organic polymer solution

without using new specially designed monomers or polymers. In the early stage of polymer hybrid development, however, only hydrophilic polymers with a high affinity to an inorganic metal oxide such as silica gels are generally used in the latter method. Since hydrophobic polymers have a very weak intermolecular interaction between the polymer and hydrophilic inorganic matrix, it is difficult to obtain homogeneous hybrids using hydrophobic polymers. Since Tamaki et al. [5] reported on the synthesis of polystyrene and silica gel polymer hybrids using  $\pi$ - $\pi$  interactions [5], transparent hybrids have been synthesized by using weak intermolecular interactions between hydrophobic polymers and inorganic matrices [6–11]. Furthermore, in recent years, interesting polystyrene composites using various inorganic oxides have been reported [12–15]. Our group synthesized transparent and homogeneous polymer hybrids using CH/ $\pi$  interactions as an intermolecular interaction that is even weaker than  $\pi$ - $\pi$  interactions [16, 17]. Tamaki's et al. [5] study was the first example of utilizing  $\pi$ - $\pi$  interactions in hybrid synthesis, although they

did not provide sufficient direct evidence that the  $\pi$ - $\pi$  interaction was involved in resulting transparent polymer hybrids. Confirming the  $\pi$ - $\pi$  interactions in the transparent polymer hybrids expands the varieties of aromatic polymers and metal alkoxides having aromatic rings for the synthesis of transparent organic-inorganic polymer hybrids, which should lead to obtain high-performance polymer hybrids.

Thus, in this study, we synthesized organic-inorganic polymer hybrids from polystyrene and phenyltrimethoxysilane via  $\pi$ - $\pi$  interactions to obtain direct evidence of the interactions based on spectroscopic characterization (Figure 1). Specifically, FT-IR and UV-vis measurements of the resulting polymer hybrids suggested that the  $\pi$ - $\pi$  interaction contributed to the formation of these transparent polymer hybrids. Until now, using FT-IR and UV-vis spectra, there has never been a direct demonstration that  $\pi$ - $\pi$  interactions contribute to the formation of these transparent polymer hybrids, and this is a very novel study. Investigating the contribution of  $\pi$ - $\pi$  interactions in organic-inorganic polymer hybrids using FT-IR or UV-vis spectroscopy will be an important way to know whether hybrids can be synthesized between various organic polymers having aromatic groups and silica gel. This novel method will be expected to be a very simple method for determining the success of hybrid synthesis. The specific results are described below.

## 2. Materials

Polystyrene (average MW 35,000) (PSt) was purchased from Sigma-Aldrich, Inc. Phenyltrimethoxysilane (PhTMOS) and methyltrimethoxysilane (MeTMOS) were purchased from Tokyo Chemical Industry Co., Ltd. 0.1 M hydrochloric acid (HCl) aqueous solution, tetrahydrofuran (stabilizer free), and liquid paraffin were purchased from Fujifilm Wako Pure Chemical Co, Ltd.

## 3. Measurements

Thermal analyses were performed on Seiko Instruments TG/DTA200. A 10% weight loss temperature ( $T_{d10}$ ) was determined by thermogravimetric analysis (TGA) at a heating rate of 10°C/min in air. Scanning electron microscopy (SEM) measurements were conducted using a JEOL JSM-5310LV system. FT-IR spectra were measured on a JASCO FT/IR-4200 spectrometer (resolution: 1 cm<sup>-1</sup>). UV-vis spectra were measured on a JASCO V-730 iRM UV-vis/NIR spectrophotometer (spectral bandwidth: 1.0 nm). After grinding the sample for 20–30 min using an agate mortar, 0.1 mg of the sample was dispersed in 0.1 mL of liquid paraffin on a quartz plate (FQ-38-13-1, manufactured by Pier Optics Co. Ltd.), and the sample was sandwiched between the quartz plates for UV-vis measurements.

## 4. Synthesis of Organic-Inorganic Polymer Hybrids from PSt and PhTMOS (Typical Procedure)

Polymer hybrid synthesis was carried out by slightly modifying the method of Tamaki et al. [5]. Specifically, the polymer hybrid was synthesized by the following method.

PSt (0.50 g) and PhTMOS (0.50 g) were dissolved in 20 mL of THF. Subsequently, 0.045 mL of 0.1 M HCl aqueous solution was added. The mixture was stirred at room temperature for 1 hr, then placed in a vessel covered with wiping paper and left in air at 80°C for 2 weeks. The obtained polymer hybrids were dried in vacuo at 60°C for 2 days.

## 5. Results and Discussion

Organic-inorganic polymer hybrids were synthesized using PSt and an alkoxysilane such as PhTMOS or MeTMOS by referring to the method of Tamaki et al. [5] (Scheme 1). The mass ratio of alkoxysilane to PSt varied, as 10 : 0, 10 : 1, 10 : 5, and 10 : 10 (Table 1). Homogeneity of the obtained polymer hybrids was evaluated optically. The optical images of the obtained polymer hybrids are shown in Figure 1. Optically transparent film was obtained from PSt without any alkoxysilanes (run 1). When the polymer hybrid was synthesized from PSt and PhTMOS, both having aromatic rings in their structures, and when the ratio of PSt : PhTMOS was 10 : 1, a transparent polymer hybrid was obtained (run 2). Transparent hybrids would be obtained by the  $\pi$ - $\pi$  interactions between the PSt and PhTMOS matrices. When the mass ratio of PhTMOS to PSt was increased to 10 : 5 or 10 : 10, the obtained polymer hybrids became translucent (runs 3 and 4). In contrast, when the polymer hybrids were synthesized using PSt and MeTMOS, which does not have an aromatic ring, the samples became turbid, indicating a phase separation of the organic and inorganic domains (runs 5 and 6). Therefore, it is strongly suggested that the  $\pi$ - $\pi$  interactions between organic polymers and the inorganic matrices play an important role in the transparency and homogeneity of the hybrids. The ability to transparently mix PSt and silica gel could be a useful method for producing high refractive index polystyrene in the future.

$T_{d10}$  of the samples was measured by TGA (Table 1).  $T_{d10}$  of pristine PSt was observed at 331.6°C while that of the polymer hybrid prepared from PSt and PhTMOS at a 10 : 1 ratio was observed at 327.0°C. This temperature is 4.6°C lower than that of pristine PSt. Invasion of the inorganic matrix into the PSt domain might disrupt the packing of PSt. As a result,  $T_{d10}$  of the hybrid prepared from PSt and PhTMOS would be lower than that of PSt. It is notable that  $T_{d10}$  tended to increase with higher silica content in the hybrid. In the case of samples prepared from PSt and MeTMOS, the same tendency as that of the polymer hybrids prepared from PSt and PhTMOS was observed.

Homogeneity of the resulting polymer hybrids was examined by SEM (Figure 2). In the cases of pristine PSt and transparent polymer hybrid (runs 1 and 2), silica domains could not be observed at the micrometer level. Thus, PSt and silica matrix generated from PhTMOS were homogeneously mixed at the molecular level [5]. However, the translucent samples (runs 3 and 4) having a higher inorganic content than that of run 2 showed a phase separation of PSt and silica derived from PhTMOS. The high inorganic content induced a phase separation in the polymer hybrid. On the other hand, in the cases of

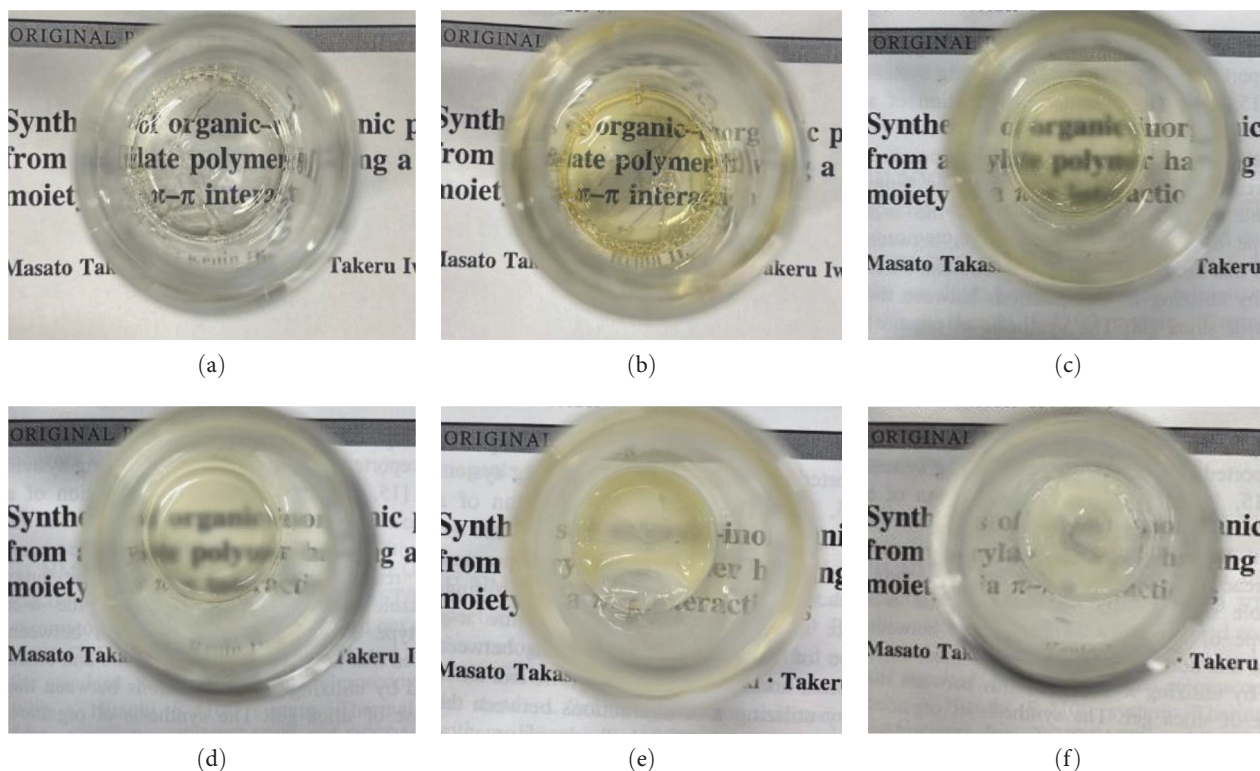
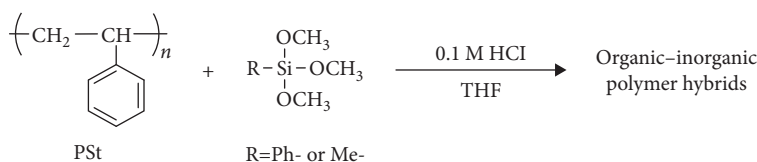


FIGURE 1: Optical images of (a) PSt:PhTMOS = 10:0 (run 1), (b) PSt:PhTMOS = 10:1 (run 2), (c) PSt:PhTMOS = 10:5 (run 3), (d) PSt:PhTMOS = 10:10 (run 4), (e) PSt:MeTMOS = 10:1 (run 5), and (f) PSt:MeTMOS = 10:10 (run 6).



SCHEME 1: Synthesis of PSt-silica hybrids utilizing  $\pi$ - $\pi$  interactions.

TABLE 1: Synthesis of PSt-silica hybrids.

Run	PSt (g)	PhTMOS (g)	MeTMOS (g)	0.1 M HCl aq. (mL)	PSt/RSi (OMe) <sub>3</sub> (w:w)	Appearance	$T_{d10}$ (°C)
1	0.5002	—	—	—	10:0	Transparent	331.6
2	0.4995	0.0494	—	0.045	10:1	Transparent	327.0
3	0.5040	0.2501	—	0.045	10:5	Translucent	328.2
4	0.4986	0.4953	—	0.078	10:10	Translucent	333.0
5	0.4991	—	0.0497	0.045	10:1	Turbid	328.0
6	0.5039	—	0.5045	0.078	10:10	Turbid	343.6

runs 5 and 6, phase separation obviously appeared in the turbid samples prepared from PSt and MeTMOS.

Homogeneity of the polymer hybrid from PSt and PhTMOS was confirmed by SEM observations. We further characterized the interaction in the polymer hybrid by FT-IR measurements. The FT-IR spectra of the samples derived from PSt and PhTMOS are shown in Figure 3. In the FT-IR spectrum of pristine PSt (run 1), absorption peaks attributed to C-H wagging vibration were observed at 842.3 and 698.1  $\text{cm}^{-1}$ . These

two peaks were also clearly observed in the spectrum of PSt:PhTMOS = 10:1 (run 2), which was synthesized from PSt and PhTMOS. These peaks, however, shifted to 841.8 and 697.1  $\text{cm}^{-1}$ , respectively, in the polymer hybrid. Furthermore, these peaks shifted to 840.8 and 696.9  $\text{cm}^{-1}$  as the silica content in the hybrids increased (runs 3 and 4). Thus, a red shift of the absorption peaks attributed to C-H wagging vibration was observed in the polymer hybrid. Zhang et al. [18] reported that the red shift of C-H wagging vibration of



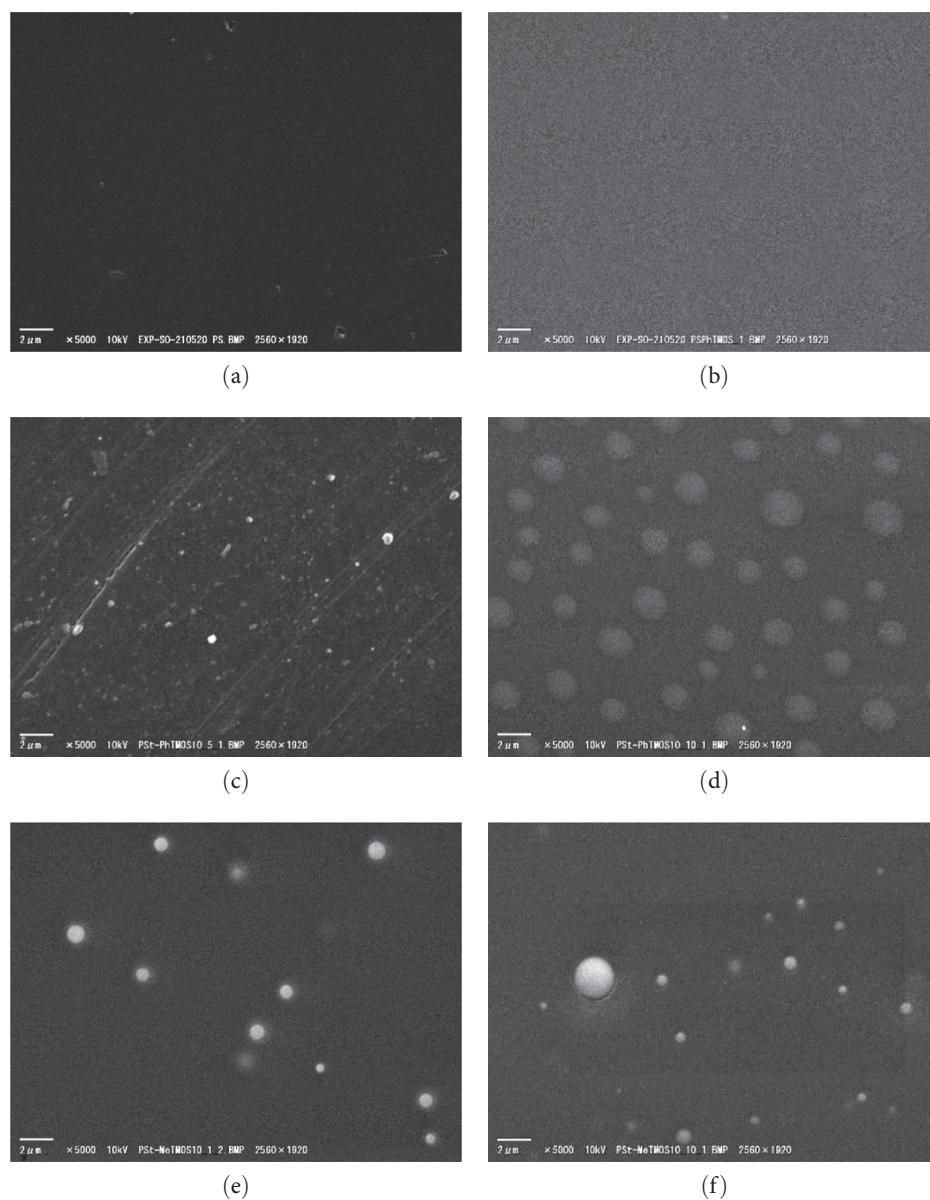


FIGURE 2: SEM images of (a) PSt:PhTMOS = 10:0 (run 1), (b) PSt:PhTMOS = 10:1 (run 2), (c) PSt:PhTMOS = 10:5 (run 3), (d) PSt:PhTMOS = 10:10 (run 4), (e) PSt:MeTMOS = 10:1 (run 5), and (f) PSt:MeTMOS = 10:10 (run 6).

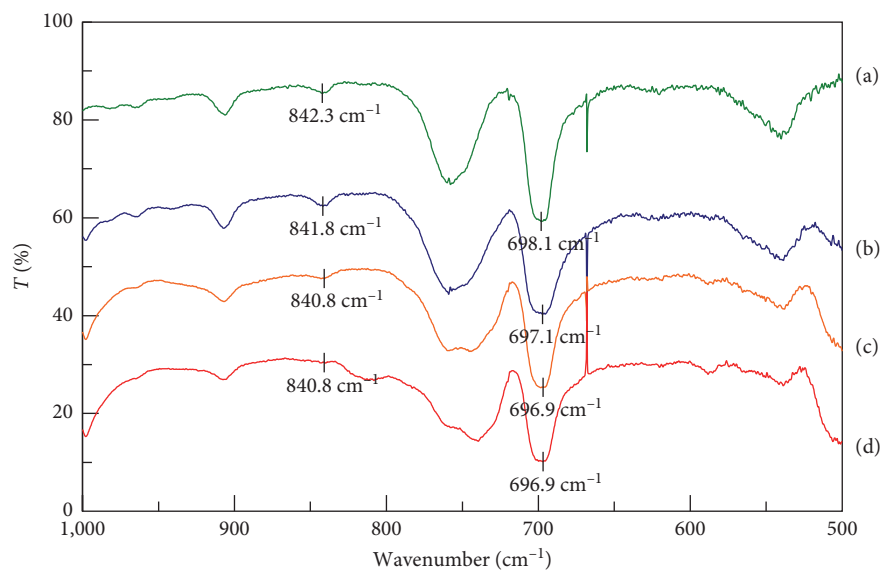


FIGURE 3: FT-IR spectra of (a) PSt:PhTMOS = 10:0 (run 1), (b) PSt:PhTMOS = 0:1 (run 2), (c) PSt:PhTMOS = 10:5 (run 3), and (d) PSt:PhTMOS = 10:10 (run 4).

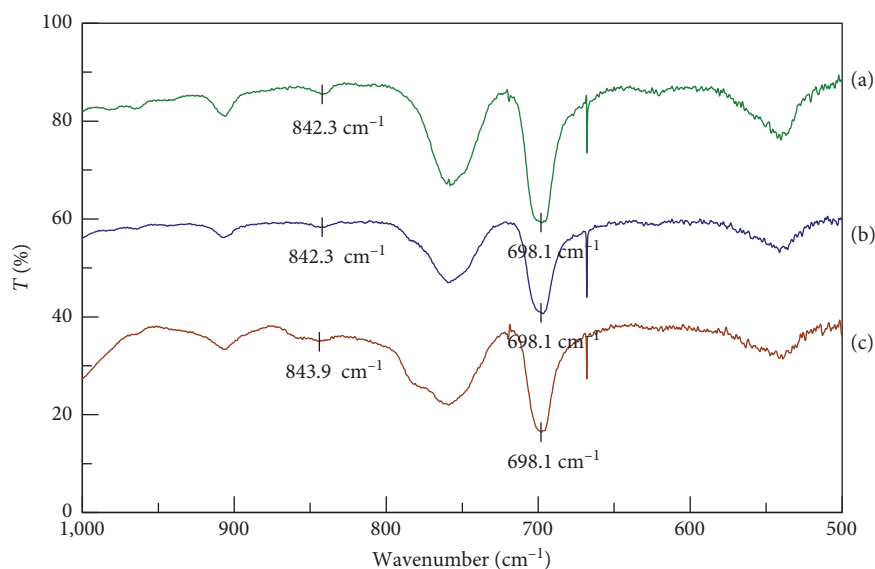


FIGURE 4: FT-IR spectra of (a) PSt:PhTMOS = 10:0 (run 1), (b) PSt:MeTMOS = 10:1 (run 5), and (c) PSt:MeTMOS = 10:10 (run 6).

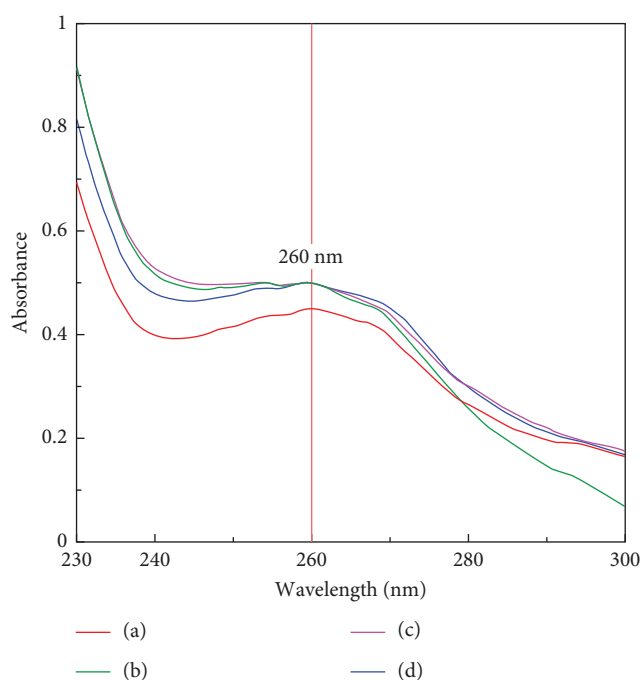


FIGURE 5: UV-vis spectra of (a) PSt:PhTMOS = 10:0 (run 1), (b) PSt:PhTMOS = 10:1 (run 2), (c) PSt:PhTMOS = 10:5 (run 3), and (d) PSt:PhTMOS = 10:10 (run 4).

aromatic compounds was due to the  $\pi$ - $\pi$  interaction. Therefore, the red shift observed in the PSt and PhTMOS hybrids indicates that the  $\pi$ - $\pi$  interaction formed between the aromatic ring of PSt and the aromatic ring of the PhTMOS matrix.

On the other hand, in the case of the samples derived from PSt and MeTMOS, absorption peaks were observed at around 842.3 and 698.1  $\text{cm}^{-1}$ , i.e., the abovementioned red shift was not observed (Figure 4). Consequently, molecular

interactions such as the  $\pi$ - $\pi$  interaction did not form between PSt and the MeTMOS matrix. These results strongly indicate that the homogeneity of the polymer hybrid was indeed achieved by the  $\pi$ - $\pi$  interaction between PSt and PhTMOS.

UV-vis spectra of the obtained hybrid were measured after further characterization of the  $\pi$ - $\pi$  interaction (Figure 5). The UV-vis spectrum of pristine PSt showed a shoulder peak at around 260 nm (Figure 5(a)) [19]. The tail of absorption tended to expand toward the long wavelength side as silica content in the hybrids increased. Generally, bathochromic shifts, which are shifts in the absorption spectrum toward the long wavelength side, are observed when the conjugated system is chemically elongated or when mobility of the  $\pi$  electron is increased [20]. Han et al. [21] characterized the  $\pi$ - $\pi$  interaction in composites of graphene and polystyrene block copolymer by a 5 nm shift to a higher field in the UV absorption peak compared to pure polystyrene block copolymer, noting that this shift originated from the effect of ring currents in graphene and polystyrene block  $\pi$ -systems [21]. Therefore, it can be concluded that the  $\pi$ - $\pi$  interaction formed in the PSt-PhTMOS hybrid samples, resulting in bathochromic shifts in the UV-vis spectrum.

## 6. Conclusions

We explored the contribution of  $\pi$ - $\pi$  interactions in the formation of polystyrene and silica gel polymer hybrids. In the FT-IR spectra, the hybrid samples derived from PSt and PhTMOS showed a shift toward low wavenumber due to the  $\pi$ - $\pi$  interaction, whereas the samples derived from PSt and MeTMOS did not show this shift. Additionally, in the UV-vis spectra of the obtained hybrid, bathochromic shifts of 5 nm due to the  $\pi$ - $\pi$  interaction between PSt and the PhTMOS matrix were observed. These results indicate that  $\pi$ - $\pi$  interactions contribute to the formation of transparent and homogeneous polymer hybrids.

Synthetic polymers derived from fossil fuels should be used as much as possible from the viewpoint of reducing their environmental impact, and disposal by incineration of these polymer materials should be avoided. However, when polymer materials are continuously used or recycled, their properties such as strength will decrease due to deterioration. In such cases, the addition of inorganic compounds to organic polymers to synthesize organic–inorganic polymer hybrids may be one method for the effective long-term use of polymer compounds. The results of this study will be expected to designs and characterizations of transparent hybrids synthesized from organic polymers having aromatic rings such as polyimide and polyamide and inorganic compounds. In the future, it will become increasingly important to utilize weak intermolecular interactions such as  $\pi$ – $\pi$  interactions.

### Data Availability

All the data required are available within the manuscript and supplementary material.

### Conflicts of Interest

The authors declare that there are no conflicts of interest.

### Acknowledgments

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### Supplementary Materials

Figures S1–S6 show TG/DTA profiles of the obtained polymer hybrids (runs 1–6). (*Supplementary Materials*)

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