



# Transition of phase-separated PBTPA/PMMA solution droplets from core–shell to Janus morphology under UV light irradiation

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## Abstract

Here, we report the morphological transition of a phase-separated structure from core–shell to Janus morphology in droplets consisting of a poly(4-butyltriphenylamine) (PBTPA)/poly(methyl methacrylate) (PMMA) blend solution, induced by UV light irradiation. We obtained a phase-separated structure formed by the evaporation of the solvent from polymer solution droplets dispersed in an aqueous solution containing a surfactant. The rate of transition decreased with increasing polymer concentration and diameter of the droplet. It was also found that the transition was caused by UV light with a wavelength of 365 nm, which is mainly absorbed by PBTPA, indicating that this phenomenon is triggered by PBTPA. When the droplet was heated to 75 °C, no transition was observed.

## Introduction

The solvent evaporation method, in which polymer particles are formed by the evaporation of the solvent from polymer solution droplets dispersed in an aqueous solution containing a surfactant, is a practical way to fabricate polymer particles [1–3]. This method is applicable to various polymers because it does not require a polymerization process. When more than two types of polymer are dissolved in the solution, polymer composite particles with various morphologies, including core–shell, Janus and dumbbell-like structures, can be obtained. These unique structures result from the phase separation of polymers or polymer solutions. The effects of several factors on the morphology, including the solvent [4], the concentration of the surfactant [5], and the molecular weight [6] and composition [7] of

the polymers, have already been investigated for conventional polymers, such as polystyrene and poly(methyl methacrylate) (PMMA). We also studied the phase separation observed in toluene solution droplets of poly(4-butyltriphenylamine) (PBTPA), which is one of the analogs possessing superior semiconducting properties [8–11], and PMMA [12]. We accidentally found that the phase-separated core–shell structure was converted to a Janus-type structure during fluorescence microscopy observations. Studies on the fabrication and structural control of polymer particles utilizing UV light irradiation have also been reported [13, 14]. However, to our knowledge, there are few studies about the transition of phase-separated structures induced by UV light irradiation. In this study, the effects of various factors, including the concentration of the polymers and the diameter of the droplets, on the UV-induced morphological transition were investigated.

## Experimental procedures

Polymer blend solution droplets were prepared by the following method. PBTPA and PMMA were dissolved in chloroform or toluene at a total concentration of 3 wt% (weight ratio = 1:1) (total 1.5 mL). The homogeneous solution was dispersed in poly(vinyl alcohol) (PVA) aqueous solution (10 mL, 0.6 wt%) using a homogenizer at 25,000 rpm for 5 s in a test tube (115 mL, i.d. = 2.7 cm). Then, the resulting dispersion was stirred at 100 rpm at room temperature to evaporate the solvent. A small portion

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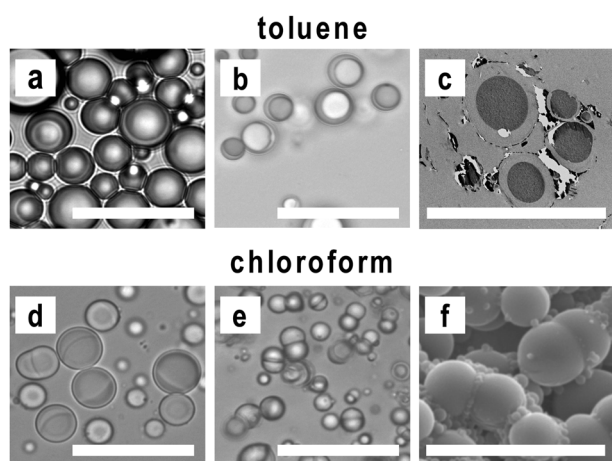
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of the dispersion (ca. 0.1 mL) was withdrawn after varying intervals and placed on a glass slide sandwiched with a cover-glass for optical micrograph (OM) observations. The concentration of the polymer was monitored by  $^1\text{H}$  NMR in  $\text{D}_2\text{O}$ . The morphologies of phase-separated PBTPA/PMMA droplets were observed by OM with or without UV light (365 nm) irradiation from a UV lamp with a bandpass filter attached to the microscope.

## Results and discussion

Figure 1 shows OM images of polymer blend solution droplets during evaporation and TEM and SEM images of particles obtained without UV light irradiation. When toluene was used as a solvent (Fig. 1a–c), a core–shell structure was observed for the droplets during the evaporation of the solvent and for the resulting particles, which consisted of a PBTPA core and PMMA shell, as confirmed by TEM. In chloroform solution (Fig. 1d–f), a Janus structure was observed at the beginning of phase separation. The morphology changed to a dumbbell-like structure with the evaporation of chloroform.

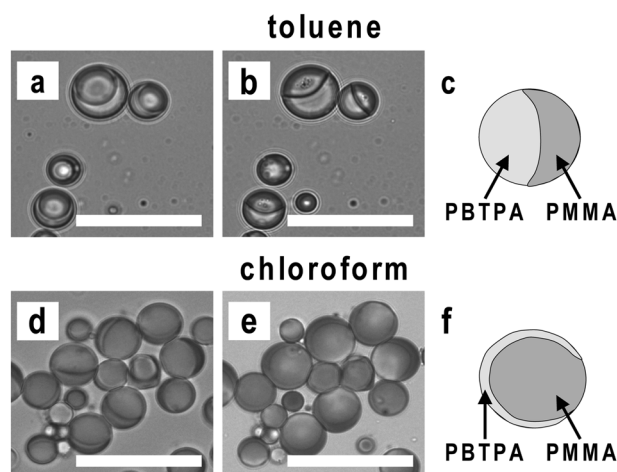
Intriguingly, as shown in Fig. 2, exposure to UV light (365 nm) changed the phase-separated morphology from the core–shell structure formed in toluene to the Janus structure (Fig. 2a–c). Fluorescence imaging of the solution droplets also showed the transition from core–shell to Janus structure during irradiation with UV light (Fig. S3). When chloroform was used as the solvent (Fig. 2d–f), the originally formed Janus structure changed to the specific structure in which the PBTPA phase surrounded the PMMA phase, as shown in the schematic representation in Fig. 2f.



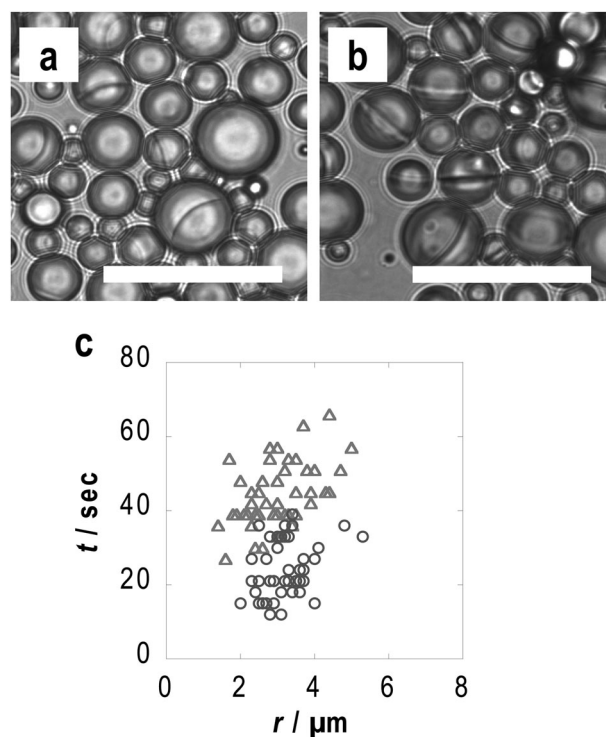
**Fig. 1** OM images of (a) toluene and (d) chloroform solution droplets dissolving PBTPA and PMMA without UV light irradiation. (b, e) OM, (c) TEM and (f) SEM images of resulting particles from (b, c) toluene and (e, f) chloroform solution droplets. All scale bars represent 10  $\mu\text{m}$

The resulting morphologies were sustained for at least 1 h after turning off the UV irradiation.

Figure 3a, b shows the UV light irradiation-induced transition in toluene solution droplets with concentrations of 7 and 13 wt%, as determined by  $^1\text{H}$  NMR. The resulting



**Fig. 2** OM images of (a, b) toluene and (d, e) chloroform solution droplets dissolving PBTPA and PMMA (a, d) before and (b, e) after UV light irradiation. Schematic graph of droplets after the transition in (c) toluene and (f) chloroform solution droplets. Yellow, PBTPA; blue, PMMA. All scale bars represent 10  $\mu\text{m}$

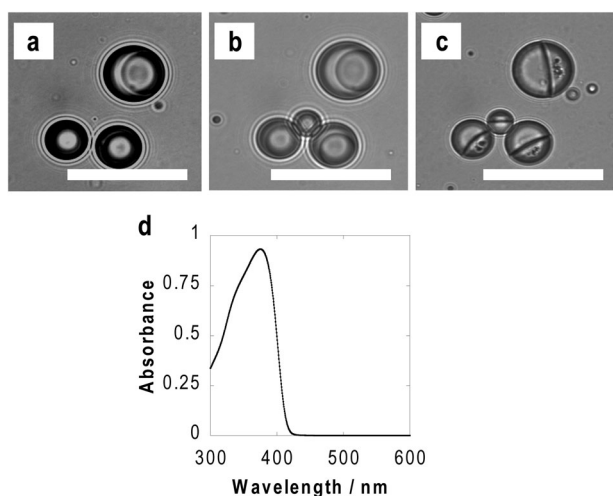


**Fig. 3** OM images of toluene solution droplets dissolving PBTPA and PMMA after UV irradiation. The polymer concentrations are (a) 7 and (b) 13 wt%, respectively. (c) Time  $t$  required to complete the structure transition as a function of diameter  $r$ . Circles and triangles represent 7 and 13 wt%, respectively. All scale bars represent 10  $\mu\text{m}$

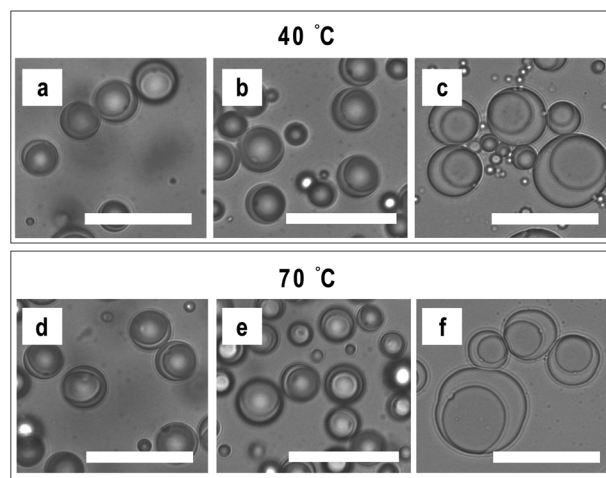
droplets had a Janus structure regardless of the concentration. The rate of transition was dependent on the concentration. To measure the time required to complete the transition, we shot sequential photographs during the UV irradiation of  $\sim 50$  droplets, as shown in Fig. S7. We compared the morphology on micrographs recorded every 3 s after the start of irradiation and determined the point when the droplet stopped changing its shape. We defined this point as the time  $t$  required to complete the transition. Figure 3c shows the time  $t$  as a function of diameter  $r$ . The solution droplets exhibited a broad size distribution under  $10\ \mu\text{m}$  (Fig. S8). The time increased with the polymer concentration. The limited translational motion of polymer chains in droplets with higher concentrations due to the higher viscosity may result in a prolonged time. The time also increased with the diameter of the particle. The transition from core-shell to Janus structure in a droplet with a larger diameter requires the mass transport of the polymer chains over a longer distance.

Figure 4a–c shows the wavelength dependence of the structural change in PBTPA/PMMA/toluene droplets after irradiation with UV light for 4 min, where long (530–550 nm) and short wavelengths (365 nm) were utilized. No significant transition was detected after exposure to UV light with the longer wavelength. However, an obvious change was observed after exposure to UV light with the shorter wavelength. As displayed in Fig. 4d, PBTPA shows an absorption spectrum in the wavelength range of 270–430 nm. This dependence indicates that the formation of the anisotropic structure induced by UV light originates from the PBTPA phase.

We assumed that the heat generated by the UV lamp causes this structural transition. To clarify the effect of heat,



**Fig. 4** OM images of toluene solution droplets dissolving PBTPA and PMMA (a) before and after irradiation with UV light for 4 min at (b) 530–550 nm and (c) 365 nm. (d) UV–vis spectrum of PBTPA toluene solution ( $1\ \text{mg L}^{-1}$ ). All scale bars represent  $10\ \mu\text{m}$



**Fig. 5** OM images of toluene solution droplets dissolving PBTPA and PMMA heated to (a–c) 40 or (d–f) 75 °C for (a, d) 0, (b, e) 1, or (c, f) 8 min. All scale bars represent  $10\ \mu\text{m}$

the dispersion was placed on a hot plate set at 40 and 75 °C. However, no transition was observed after heating, as shown in Fig. 5. Therefore, UV light at 365 nm causes the structural transition from core-shell to Janus in polymer blend solution droplets.

Triphenylamine (TPA) derivatives have been utilized as hole transporters in a variety of applications and are known as photoconductors [15, 16]. Photoconductive materials absorb light to generate free carriers. Similar to other TPA derivatives, PBTPA chains absorb UV light to transition to the excited state [17] and are subsequently oxidized by electron transfer to the surrounding medium, such as toluene and water. The formation of trace amounts of radical cations changes the solution characteristics [18], altering the nature of the interface and reorganizing the phase-separated structure. The morphology of polymer blend particles is thermodynamically determined to minimize the total interfacial free energy, represented as interfacial tension [19]. The hydrophobicity of the polymer also affects the shape of the droplet [20]. The UV light irradiation in the present work implies a change in the interfacial tension and hydrophobicity between the polymer and aqueous phase. As a result, the droplet morphology changes from core-shell to Janus to minimize the total free energy by increasing the interfacial area between the PBTPA-rich phase, which possesses an ionic or hydrophilic nature, and the aqueous phase.

## Conclusions

In summary, UV light at 365 nm causes the unexpected structural transition from core-shell to Janus in PBTPA/PMMA blend solution droplets. The rate of structural

transition slowed down with increasing polymer concentration and increasing diameter, suggesting that the mass transfer is the rate-determining step. No transition was induced by light at 530–550 nm. This dependency on the wavelength of UV light indicates that the transition originates from light absorption by PBTPA. Although the droplet was heated to 75 °C, no transition was observed.

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### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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