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Diameter control of poly(p-oxycinnamoyl) microspheres prepared by self-organizing polycondensation

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Abstract

The diameter control of poly(p-oxycinnamoyl) (POC) microspheres was examined. POC microspheres were prepared by the polycondensation of (E)-4-acetoxycinnamic acid in liquid paraffin at 320 °C. The microspheres were formed through the formation of microdroplets by the reaction-induced liquid–liquid phase separation and the subsequent polymerization of oligomers in the microdroplets leading to the solidification. The size of the microspheres was actually governed by the coalescence of the microdroplets in the growth process. In order to control the coalescence of the microdroplets, 4-octadecyloxybiphenyl (ODB) was added to the polymerization solution as a coalescence inhibitor, which exhibited amphiphilicity to liquid paraffin and POC. ODB inhibited the coalescence of the microdroplets. The average diameter decreased with the increase of the ODB concentration, and it was tunable from 0.97 to 4.61 μm.

Keywords: Aromatic polyester; Microspheres; Phase separation

1. Introduction

Poly(p-oxycinnamoyl) (POC) is a rigid-rod aromatic polymer comprised of p-vinylphenyl group and ester linkage, and expected to possess many excellent properties such as thermal stability, mechanical properties and chemical resistance. However, POC shows neither fusibility nor solubility due to the strong enthalpic interaction and the minimal increase in conformational entropy associated with its dissolution or melting. Therefore, the intractability derived from the rigid-rod chain structure makes POC inaccessible for processing by conventional techniques. Copolymers containing p-oxycinnamoyl unit had been prepared to improve the above intractability and their thermotropicity was examined [1,2].

We have been studying on the morphology control of rigid polymers during polymerization to overcome the trade-off relationship between properties [3–6] and precessability, and succeeded in preparing POC microspheres [7–9]. The POC microspheres were obtained by the self-organizing polycondensation of (E)-4-acetoxycinnamic acid (ACA) in liquid paraffin and other aromatic solvents, as illustrated in Scheme 1. The POC microspheres have been receiving much attention as high performance microspheres. The microspheres are formed through the formation of the microdroplets by the reaction-induced liquid–liquid phase separation of oligomers and the subsequent polymerization in the microdroplets leading to the solidification due to the increase of molecular weight. They are grown by not only the consecutive supply of the oligomers from the solution but also the coalescence of the microdroplets.

The diameter control of microspheres is of great importance to use them as industrial materials, and the very fine particles have been desired from the view of the nano-scale technology. This paper describes our new findings on the diameter control of POC microspheres.

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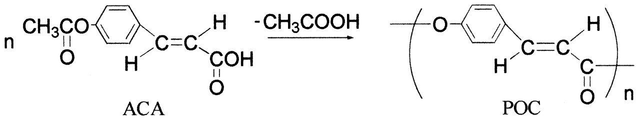

Scheme 1. Synthesis of POC from ACA.

2. Experimental section

2.1. Materials

ACA was synthesized according to the previous reported procedure [1,2]. 4-*n*-octadecyloxybiphenyl (ODB) was purchased from TCI Co. Ltd and purified by recrystallization from toluene. Liquid paraffin was purchased from Nacalai Tesque Co. Ltd and purified by vacuum distillation (220–240 °C/0.3 mmHg). Therm-S 900 (TS9), which was the mixture of hydrogenated terphenyl, was purchased from Nippon Steel Chemical Co. Ltd and purified by vacuum distillation (150–170 °C/0.7 mmHg)

2.2. Polymerization

The typical polymerization procedure was described as follows. Into a cylindrical vessel equipped with a mechanical stirrer and a gas inlet tube were placed ACA (0.30 g, 1.46 mmol) and 20 ml of liquid paraffin (1.5 wt/vol% based on monomer weight and solvent volume). The reaction mixture was heated under a slow stream of nitrogen up to 320 °C with stirring. The stirring was stopped when ACA was completely dissolved. The temperature was maintained at 320 °C for 6 h. The precipitated products were collected by vacuum filtration at 320 °C, and washed with *n*-hexane and acetone. Product characteristics were as follows. FT-IR (KBr) (cm^{-1}): 2920 (aromatic CH), 1725 (ester C=O), 1633 (vinyl C=C). Anal. calcd for $C_9H_6O_2$: C, 73.97; H, 4.14; O, 21.89. Found: C, 75.00; H, 4.21; O, 20.79.

2.3. Measurements

The diameter of the microspheres was determined by the average of over 200 observation values on scanning electron microscope S-2150, Hitachi Co. Ltd. FT-IR spectra were measured on FT/IR-410, JASCO Co. Ltd. Solid-state ^{13}C NMR was measured on Bruker AVANCE500 operating at 75 MHz. The densities of the microspheres were measured by the floatation method using tetrachloromethane and *p*-xylene at 25 °C.

2.4. Analysis of DOB content in POC microspheres

Sample (10 mg) and 1 ml of 7.0 wt% KOH methanol solution were placed in a tube and hydrolyzed at 25 °C until the sample was completely hydrolyzed. The solution was neutralized with dilute hydrochloric acid and then analyzed by using gas chromatography (GC) with GC-14B Shimadzu Co. Ltd with FID equipped with a Thermon-3000 (60–80 mesh) packed column. Column was heated at a rate of 5 °C min^{-1} from 80 to 270 °C and then maintained at 270 °C. Injection and detection temperature were 280 and 290 °C, respectively.

3. Results and discussion

As previously reported [7–9], the POC microspheres are formed according to the following mechanism. When the molecular weight of oligomers increases in the solution by condensation reaction, they are phase-separated from the super-saturated state by liquid–liquid phase separation. The microdroplets of dense phase are formed in the dilute solution. This reaction-induced liquid–liquid phase separation is the binordal decomposition, not spinordal decomposition, and the formation of the microspheres is the nucleation and growth mechanism. The generated microdroplets are gradually grown by not only the consecutive supply of oligomers from solution phase but also the coalescence of them. The concentration of oligomer is quite high in the microdroplets, and therefore the further polymerization occurs rapidly in them. The crystallization, so-called solidification, is induced in the microdroplets by the increase of the molecular weight of oligomers. This solidification leading to the stabilization of the surface stops the coalescence of the microdroplets, and the microspheres are eventually formed. Although the phase-separation of oligomers and further polymerization between oligomers in the microdroplets are important process in the formation of POC microspheres, this formation mechanism resembles primarily that of the precipitation polymerization of vinyl monomers, which is nucleation and growth. Therefore, it seems likely that the diameter of the microspheres is governed by the nucleation process and the growth process. With respect to the nucleation process, the number of nuclei is a controllable factor. It is well known that the critical radius of nucleus (r^*) and nucleation rate (J) depend on the degree of super-saturation as follows [10,11].

$$\Delta\mu = kT\ln(1+\sigma) \qquad \sigma = (C - C_e)/C_e$$

$$r^* = 2v\gamma/\Delta\mu$$

$$J = \nu_+ q\exp(-\Delta G^*/kT) = \nu_+ q\exp(-16\pi\gamma^3 v^2/3\Delta\mu^2 kT)$$

where μ, chemical potential; C, concentration of solute; C_e, equilibrium concentration r^*, critical radius of nucleus; v, volume of molecule; γ, density of surface energy; J, nucleation rate; ν_+, rate of crystallization of one molecule into critical nucleus; q, density of free molecule.

When the degree of super-saturation (σ) increases, $\Delta\mu$ which is a driving force for nucleation becomes larger. This large $\Delta\mu$ leads to small r^* and large J, indicating that the much more nuclei having smaller radius are formed. The σ is highly related to the miscibility between the oligomer and the solvent, and the lower miscibility results in the larger σ. The lower miscibility of liquid paraffin and the oligomer

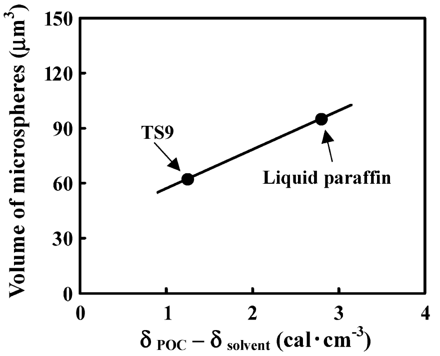

Fig. 1. Plot of average volume of microspheres as a function of difference of solubility parameter between POC and solvent.

makes the σ larger. If the diameter of the microspheres is determined by this nucleation process, the polymerization in the more miscible solvent results in the larger microspheres because the smaller number of the nuclei with the larger diameter should be generated. Fig. 1 is the plot of the volume of the microspheres as a function of the difference in the solubility parameters (δ) between POC and the solvent. The δs of liquid paraffin and TS9 are appeared in the previous study [12], and that of POC is estimated by Fedor's group contribution method [13]. Although, the miscibility of TS9 and POC is larger than that of liquid paraffin, the

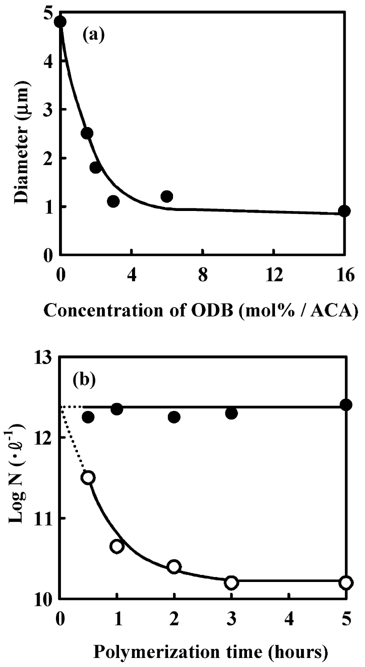

Fig. 3. Plots of (a) diameter of microspheres as a function of ODB concentration, and (b) number of microspheres prepared with the addition of ODB at the concentration of (○) 0 mol% and (●) 16.2 mol%/ACA as a function of polymerization time.

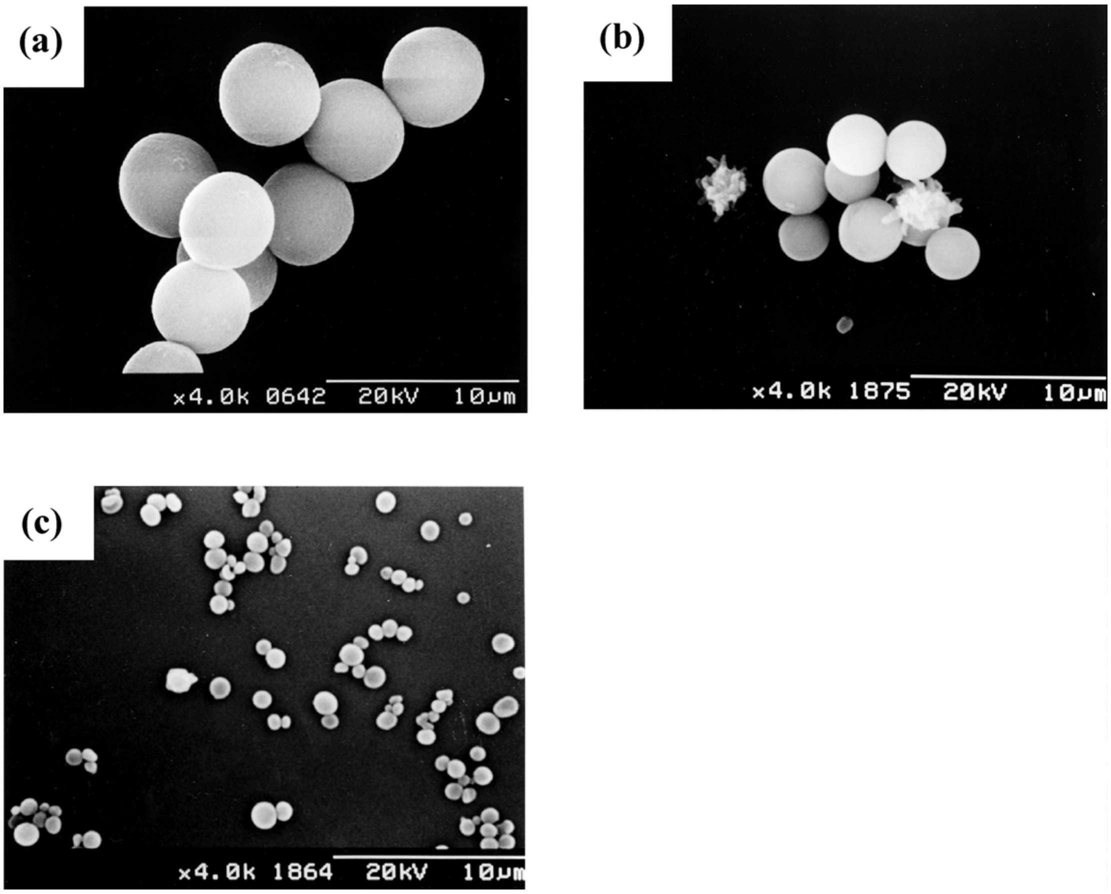

Fig. 2. POC microspheres prepared with the addition of ODB at the concentration of (a) 0 mol%, (b) 1.5 mol% and (c) 16.2 mol%/ACA.

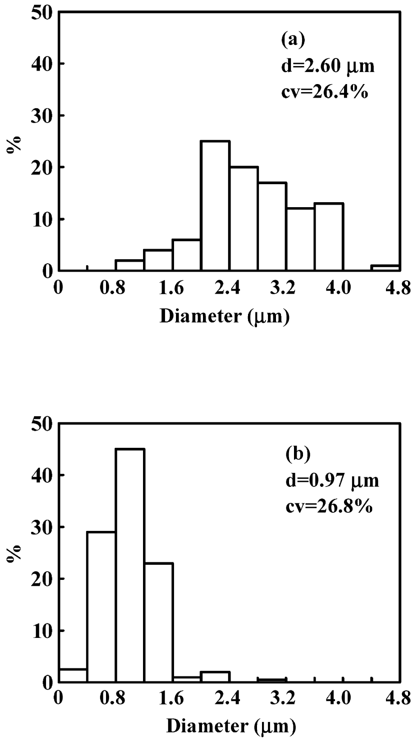

Fig. 4. Diameter distribution diagrams of microspheres prepared with the addition of ODB at the concentration of (a) 1.5 mol% and (b) 16.2 mol%/ACA.

microspheres prepared in TS9 are larger than that in liquid paraffin. This tendency is completely opposite to the above discussion. This fact indicates that the nucleation process does not influence actually the diameter of POC microspheres and the growth process including the coalescence does determine the diameter.

In order to control the coalescence process of the microdroplets, ODB is added as a coalescence inhibitor comprised of octadecyl and biphenyl moiety. Octadecyl moiety in ODB shows high miscibility to liquid paraffin and biphenyl moiety is more miscible to POC. The polymerizations of ACA were carried out in liquid paraffin with ODB at various concentrations. Figs. 2 and 3 show the microspheres and the plot of the diameter as a function of ODB concentration. The diameter of the microspheres is clearly dependent on the ODB concentration. It decreases monotonously with the increase of the ODB concentration and then levels off to 0.97 μm. Fig. 4 shows the distribution diagrams of the diameter. These microspheres exhibit broad diameter distribution, of which the coefficient of variation is ca 26% at any given concentration of ODB. ODB exhibits amphiphilicity to liquid paraffin and the oligomers, and therefore it is favorably located on the surface of the microdroplets. Long alkyl group in ODB hinders the coalescence of the microdroplets. The number of the microspheres (N) is calculated in the course of the polymerization according to the following equation

$$N = Y/(4\pi r^3 \rho/3)$$

Y, yield of microspheres; r, average radius; ρ, density of microspheres (1.38 g cm^{-3})

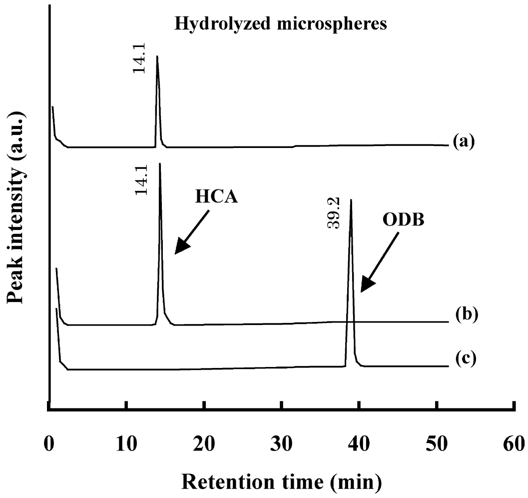

Fig. 5. GC analysis of (a) hydrolyzed microspheres prepared in liquid paraffin with the addition of ODB at the concentration of 16.2 mol%/ACA, (b) HCA and (c) ODB.

When ODB is not added, the number of the microspheres decreases rapidly at the beginning of the polymerization due to the coalescence of the microdroplets and then it becomes constant due to the solidification. In contrast to this, the number of the microspheres is almost constant during polymerization when ODB is added at the concentration of 16.2 mol% to ACA. This reveals that the coalescence between the microdroplets is inhibited by the addition of ODB and this strongly supports the above discussion. As described before, POC is not dissolved into any solvents, and hereby the content of ODB in the microspheres was analyzed on GC after the hydrolysis. Fig. 5 illustrates the results of GC analysis. The peak of HCA is detected after the hydrolyzed sample of the microspheres but that of ODB is not detected. Solid-state ^{13}C NMR was also measured to confirm the existence of ODB in the microspheres. Fig. 6 is a CP/MAS/TOSS ^{13}C NMR spectrum of the microspheres prepared in liquid paraffin with the addition of ODB at the concentration of 16.2 mol%/ACA. Only the peaks assigned for POC are clearly observed as shown in this spectrum. Any peaks of ODB are not detected. These results reveal that the microspheres do not contain ODB. ODB are excluded from the microspheres by the segregation effect while the microdroplets are solidified by the crystallization because ODB does not possess the reactive group and it is not covalently bound to the oligomers.

4. Conclusions

The average diameter of POC microspheres is predominantly determined by the coalescence of the microdroplets

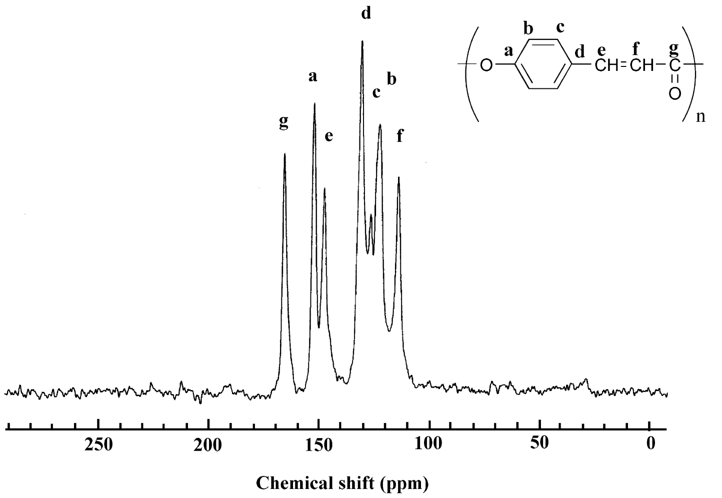

Fig. 6. CP/MAS/TOSS ^{13}C NMR spectrum of the microspheres prepared in liquid paraffin with the addition of ODB at the concentration of 16.2 mol%/ACA.

formed through liquid–liquid phase separation. ODB inhibits the coalescence and thereby the diameter decreases with the increase of the concentration of ODB.

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