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SHORT COMMUNICATION

Preparation of poly(4-butyltriphenylamine) particles by chemical oxidative dispersion polymerization

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Abstract Photoconductive poly(4-butyltriphenylamine) particles were prepared by a chemical oxidative dispersion polymerization. The utilization of statistical copolymer of methyl methacrylate with 2-hydroxyethyl methacrylate (30:70) as a dispersant afforded particles with the narrowest distribution when the other experimental conditions such as the rate of monomer feed, and the dispersant concentration were appropriately selected. Porous particles were obtained at 40 °C using poly(vinyl pyrrolidone) as a dispersant.

Keywords Photoconductive polymer ·
Chemical oxidative dispersion polymerization ·
4-Butyltriphenylamine

Introduction

Nonaqueous phase dispersion (NAD) polymerization affords polymer particles with micron order size. [1]. Polymer particles prepared by NAD polymerization have been widely used in industrial applications, such as for standard calibrations, paints, and so on. Most of these studies deal with conventional vinyl monomers such as styrene [2, 3] and methyl methacrylate [4, 5] with radical initiators.

Because the dispersion of conducting polymer provides processibility, nevertheless, the insolubility of most of the conducting polymers, chemical oxidative dispersion polymerizations of non-vinyl monomers such as pyrrole, aniline, and aniline derivatives have been reported in recent years [6–17].

Preparation of stable polymeric dispersions requires the selection of an appropriate stabilizer and solvent to provide the effective stabilization of colloidal systems and to control the morphology, particle size, and its distribution, for the chemical oxidative dispersion polymerization of pyrrole, poly(vinyl pyrroridone) (PVP), poly(vinyl alcohol-*co*-vinyl acetate) [6, 7], poly(vinyl alcohol) (PVA) [8], poly (vinyl methyl ether) [9], poly(2-(*N*,*N*-dimethylamino)ethyl methacrylate-*block*-butyl methacrylate) [10], ethylhydroxyethylcellulose [11], etc. In the case of pyrrole polymerization with PVA as a stabilizer, the rate of addition of the pyrrole monomer affected the particle size [7]. Ishizu et al. prepared polypyrrole particles by a dispersion polymerization using ferric chloride as an oxidant and PVA or that functionalized with pyrrole moiety as the stabilizer. The functionalized PVA acted not only as a stabilizer but also as a comonomer [8].

We reported that triarylamine polymers with the well-defined structure were simply prepared by a chemical oxidative polymerization using ferric chloride as an oxidant [18, 19]. Poly(4-butyltriphenylamine) (PBTPA) showed the excellent photoconductivity compared with a conventional poly(*N*-vinyl carbazole) [18]. Triphenylamine derivatives have been used as hole-transporting materials in organic photoconductors and electroluminescent devices [19, 20]. Recently, we also reported the preparation of monodispersed polystyrene/PBTPA composite particles by chemical oxidative seeded dispersion polymerization using PVP as dispersant. The effect of preparation conditions such as solvent, stabilizer, temperature on particle size, and its distribution were investigated [21]. In this study, PBTPA particles are directly prepared by chemical oxidative dispersion polymerization of BTPA (Scheme 1). The relationships between the polymerization conditions and the characteristics of resulting particles including yield,

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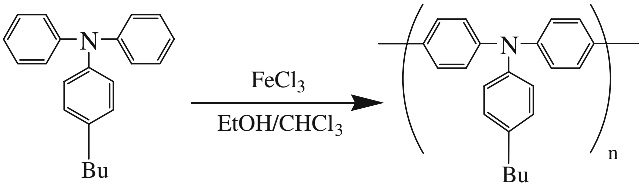

Scheme 1 Polymerization of 4-butyltriphenylamine

molecular weight, size and its distribution, and surface morphology are discussed.

Experimental

Materials

All the reagents, unless stated otherwise, were purchased from Wako Pure Chemical Industries. Xylene was distilled under atmospheric pressure. Chemicals were used without further purification otherwise noted.

Preparation of BTPA monomer

BTPA were synthesized from diphenylamine and 1-bromo-4-butylbenzene utilizing Pd-catalyzed coupling reaction as described in [18]. To a three-neck 300-ml flask equipped with a magnetic stirrer and a nitrogen inlet were added 18.9 g (0.0886 mol) of diphenylamine, 18.9 g (0.0889 mol) of 1-bromo-4-butylbenzene, 19.9 mg (0.0886 mmol) of palladium(.) acetate, and 10.2 g (0.106 mol) of *t*-BuONa. After the addition of Xylene (120 ml) and 0.1 M P(*t*-Bu)$_3$ xylene solution (3.54 ml, 0.544 mmol), the mixture was stirred at 120 °C for 3 h under nitrogen atmosphere. After cooling down to 80 °C, 100 ml of water was poured into the reaction mixture. The organic layer was washed with water and concentrated by evaporation followed by purification using column chromatography (silica, toluene/hexane) to remove by-products and unreacted materials. The white solid of BTPA was obtained (yield, 93.2%). ^{1}H NMR (500 MHz, CDCl$_3$), δ (ppm) from TMS: 7.22–6.93 (m, 14H), 2.56 (t, 2H), 1.59 (m, 2H), 1.36 (m, 2H), 0.93 (t, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) from TMS: 148.01 145.32, 137.71, 129.15, 129.07, 124.67, 123.64, 122.19, 35.04, 33.67, 22.41, 14.00.

Stabilizer

Poly(vinyl pyrrolidone) (PVP; K-30, Wako Pure Chemical Industries, Mw 40,000), and poly(ethylene oxide) (PEO, Aldrich, Mv 200,000) were utilized as received. Statistical copolymers of 2-hydroxyethyl methacrylate (HEMA) with methyl methacrylate (MMA) [poly(HEMA-*co*-MMA)s] with various chemical composition were prepared by solution polymerization at 60 °C for 24 h. HEMA, MMA (total monomer 8 g), 2,2′-azobisisobutyronitrile (AIBN) (0.08 g), and tetrahydrofuran (32 g) were charged into two-necked round bottom flask equipped with a magnet stirrer and nitrogen inlet. The mixture was degassed by freeze–thaw cycles with a liquid nitrogen bath before temperature was raised to 60 °C. After polymerization, the reaction mixture was poured into the mixture of hexane–toluene, and the precipitates were collected and dried. Number average molecular weights of statistical copolymers are in the range of 9,000–12,000, and polydispersity index (PDI) at 2.6–2.8. The chemical compositions of copolymers were almost the same as those in feed because the yields were more than 90% in all cases. It is expected that the chemical compositional distribution exists in each copolymer because reactivity ratios of two monomers are $r_{\mathrm{MMA}}=0.824$ and $r_{\mathrm{HEMA}}=0.63$ [22]. Homopolymers, PMMA, and PHEMA were prepared in a same manner.

Chemical oxidative dispersion polymerization

In a three-necked 50-ml round-bottom flask equipped with a condenser and a nitrogen inlet, ferric chloride (4 mol equivalents of monomer) and stabilizer were dissolved in ethanol/chloroform solvent mixture (2.5 ml). The monomer (2.5 mmol) was dissolved in the same solvent (2.5 ml). The monomer solution was fed to the reaction vessel after the temperature reached the desired value. Feeding rate was controlled by a syringe pump in the range from 0.025 to 0.3 ml/min. Chemical oxidative dispersion polymerizations were carried out for 24 h. Resulting particles were washed repeatedly with ethanol.

Characterizations

Morphology and particle size of resulting polymers were evaluated by scanning electron microscopy (SEM; Philips XL 30) with a 15° tilt. The average diameter of PBTPA particles and its distribution were determined by the direct measurement of 200 over particles in SEM photographs. Coefficient of variation (CV) is calculated according to the following equation: CV=*S*/*D*n, where *S* is number average diameter of PBTPA particle and *D*n is the standard deviation.

^{1}H and ^{13}C NMR spectra were recorded on chloroform-*d* solutions with tetramethylsilane (TMS) as an internal standard using a Jeol Alpha-500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz). The molecular weight of polymer was evaluated by GPC using Jasco 880-PU pump, a column packed with styrene–diviylbenzene gel beads [22], and a Jasco UV-970 detector. Chloroform was used as an eluent, and the molecular weight was calibrated with polystyrene standards.

Results and discussion

Table 1 lists the oxidative polymerization conditions and the experimental results when PVP was used as a stabilizer. At first, the effect of solvent composition (ethanol/chloroform) on particles formation was investigated (P1–P3). The products of runs P1 and P3 were spherical particles with ethanol/chloroform ratio of 7:3 and 3:7, respectively. On the other hand, nonspherical particles were obtained with an ethanol/chloroform ratio of 5:5. From these experimental results, it seems that well-balanced relationship between the polymerization rate (or the molecular weight of resulting polymer) and the critical chain length for precipitation is important to obtain spherical morphology. At the critical chain length, the resulting oligomer will precipitate from homogeneous reaction medium. In this case, the increase of ethanol content decreased the critical chain length for precipitation, as ethanol is a poor solvent for the BTPA polymer. As the content of ethanol in the reaction medium increased, the molecular weight of the resulting polymer or the rate of polymerization decreased. This is because ethanol deactivated the oxidant because of the coordination.

In the chloroform-rich medium (ethanol/chloroform, 3:7), the reactivity of monomer was high, and the critical chain length was long, and the well-balanced relationship between both parameters was established to produce the spherical particles. In the ethanol-rich medium (ethanol/chloroform, 7:3), both parameters decreased and were still well-balanced to maintain the spherical morphology. When the ratio was 5:5, the molecular weight of the resulting polymer was slightly larger than that of the ratio of 7:3. It is reasonably speculated that the increase of chloroform content from 30 to 50% increases the critical chain length to a greater extent compared with the molecular weight increase. Therefore, it is probably concluded that well-balanced relationship no longer existed in the 5:5 medium, leading to nonspherical products.

PBTPA particles were prepared at different PVP concentration (weight percent based on BTPA monomer, 5, 10, 15, 20 wt%). In conventional dispersion polymerization of vinyl monomers, the average diameter of particles generally lowers with the increasing of PVP concentration. As shown in Table 1 (runs P3–P6), the average diameter increases gradually with the increasing of PVP concentration in this system. Molecular weight increases with the increase in PVP concentration until 15 wt%. At 20 wt%, low molecular weight product was obtained with low conversion. It is considered that excess amount of PVP deactivated oxidant because of the complex formation resulting in decreasing molecular weight. The spherical particles obtained at 10, 15, and 20 wt% afforded the stable dispersion. However, the particles were coagulated where the concentration of PVP was less than 10 wt%. It seems that more than 10 wt% PVP is necessary to stabilize the dispersion of particles in this experimental condition.

PBTPA particles were prepared with various feeding rates as shown in Table 1 (runs P3 and 7–9). In our investigation, the rate of 0.05 ml/min was appropriate for particle formation, and the faster (0.3 ml/min) or slower (0.01 ml/min, 0.025 ml/min) rates afforded polydispersed or aggregated nature to the resulting particles. At 0.3 ml/min, the generation of PBTPA was so fast that too many PBTPA chains are precipitated from the medium to be adsorbed incompletely to nuclei particles. In the case of below 0.01 ml/min, nucleation stage was prolonged. Nucleation and growth process existed competitively throughout the monomer feeding. Subsequently, long feeding time leads to polydispersed particles. Tseng et al. [23] stated that the rate of nuclei generation was an important factor to obtain monodispersed particles.

Table 1 Experimental conditions and results for chemical oxidative dispersion polymerization with PVP stabilizer

Run	Solvent [a]	Feed rate (ml/min)	PVP [b] (wt%)	Reaction temperature (°C)	Diameter (μm)	CV value (%)	Mw ($\times 10^3$)	PDI	Conversion (%)
P1	3:7	0.05	10	50	1.23	32.9	12	5.8	61.4
P2	5:5	0.05	10	50	[c]	[c]	4.9	1.8	60.6
P3	7:3	0.05	10	50	0.75	22.8	3.8	1.7	60.8
P4	7:3	0.05	5	50	[c]	[c]	2.8	1.3	64.3
P5	7:3	0.05	15	50	0.89	24.8	6.6	3.5	61.2
P6	7:3	0.05	20	50	1.17	29.3	3.7	1.6	43.0
P7	7:3	0.025	10	50	0.31	67.1	4.5	2.0	60.5
P8	7:3	0.01	10	50	0.64	41.1	3.8	1.5	60.4
P9	7:3	0.3	10	50	[c]	[c]	2.8	1.5	58.0
P10	7:3	0.05	10	40	3.31	41.1	2.1	1.2	6.8
P11	7:3	0.05	10	45	2.96	39.9	2.4	1.1	24.6

[a] Ethanol/chloroform ratio, total=5 ml

[b] Weight percentage based on BTPA monomer

[c] Coagulated particles were produced.

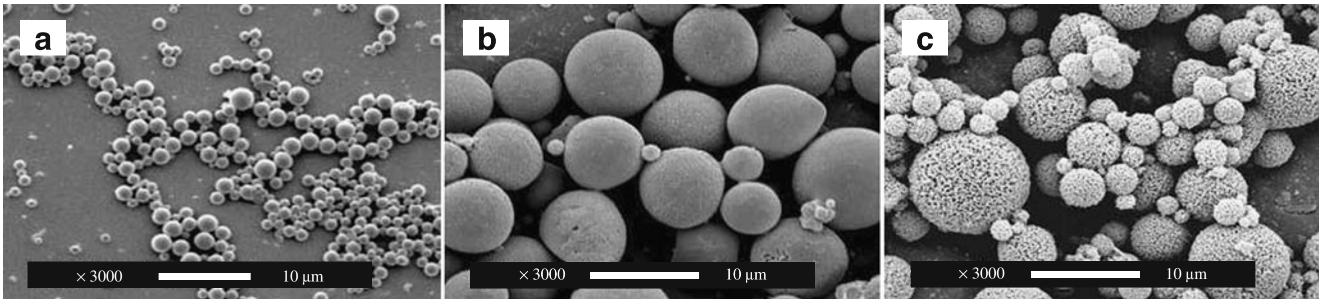

Fig. 1 SEM photographs of PBTPA particles produced by chemical oxidative dispersion polymerization using PVP as a dispersant with different reaction temperature: 50 °C (**a**), 45 °C (**b**), 40 °C (**c**)

Figure 1 shows SEM photographs of PBTPA particles prepared at different reaction temperature (40, 45, and 50 °C) with PVP as a stabilizer. The diameter of particle decreased with the increase of reaction temperature. It is considered that nuclei formation ended in earlier stage because the solvating power of solvent decreased at lower temperature. The size distribution of particle was the narrowest at 50 °C. Furthermore, porous particles were obtained at 40 °C (run P10). The porous particles seem to be formed by the coagulation of small particles during the reaction. The other possibility is that the porous nature generated at purification process. At 40 °C, lower molecular weight polymer was produced compared with at 45 and 50 °C. Especially lower molecular weight fraction was extracted by washing process, or highly swollen particles became porous during drying process.

Monodispersed particles were not obtained with PVP. Different polymers such as PEO, PMMA, PHEMA homopolymers, and MMA–HEMA statistical copolymers were examined as a dispersant (the experimental conditions are described in Table 2). When PEO, PMMA, and PHEMA were used as dispersant (10 wt% of monomer), most of resulting polymers were coagulated, and no spherical particles were obtained. These polymers have no well-balanced nature for affinity to resulting PBTPA and the continuous phase. On the other hand, spherical particles were obtained when amphiphilic MMA–HEMA statistical copolymers were used as a dispersant. Table 2 summarizes the experimental results for chemical oxidative dispersion polymerization using MMA–HEMA statistical copolymers. Solvent composition was fixed to ethanol/chloroform 7:3, as spherical particles were obtained with PVP at this composition. Feeding rate and reaction temperature were also fixed to 0.05 ml/min and 50 °C, respectively. The effect of chemical composition of statistical copolymer was investigated. SEM photographs of PBTPA particles obtained using statistical copolymers with different composition are shown in Fig. 2 (Table 2, C1–3). At higher HEMA content, the generation of secondary particles is suppressed, and the particles with narrow distribution were obtained. MMA sequence provided adsorbing site for the PBTPA chains, whereas HEMA sequence has higher affinity to the continuous phase and plays a role of steric barrier. Well-balanced composition or polarity is necessary to obtain monodisperse polymer particles.

PBTPA particles were prepared at different dispersant concentration (weight percent based on BTPA monomer, 5, 10, and 15 wt%). Figure 3 shows SEM images of the resulting particles. With increase of dispersant concentration, the average diameter decreased, and PDI became larger

Table 2 Experimental conditions and results for chemical oxidative dispersion polymerization using MMA–HEMA statistical copolymers as a dispersant

Run	MMA/HEMA ratio[a] (−)	MMA/HEMA[b] (wt%)	Diameter (μm)	CV value (%)	Mw $(\times 10^3)$	PDI	Conversion (%)
C1	70:30	5	[c]	[c]	3.5	2.4	68.0
C2	50:50	5	4.28	42.3	2.4	1.5	71.1
C3	30:70	5	4.33	13.0	2.3	1.5	70.1
C4	30:70	10	3.68	44.7	3.2	3.1	71.2
C5	30:70	15	1.95	50.0	3.5	5.2	65.0

Polymerization was carried out in ethanol/chloroform (7:3) at 50 °C. The rate of monomer feed was 0.05 ml/min.

[a] Calculated from ^{1}H-NMR and the number average molecular weight of copolymers are 12,000 (MMA/HEMA = 70:30), 10,000 (50:50), and 9,000 (30:70).

[b] Weight percentage based on BTPA monomer

[c] Coagulated particles were produced.

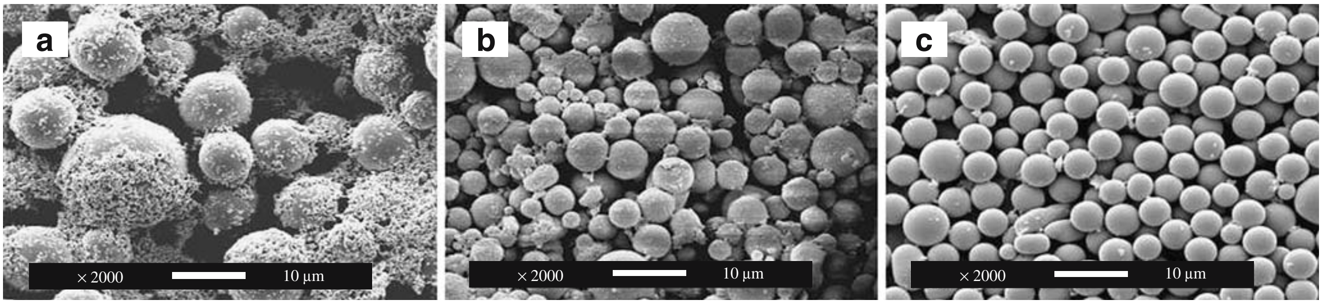

Fig. 2 SEM photographs of PBTPA particles prepared by chemical oxidative dispersion polymerization using MMA–HEMA statistical copolymers as a dispersant. MMA/HEMA ratio: 70:30 (**a**), 50:50 (**b**), and 30:70 (**c**)

(Table 2, C3–5). Larger PDI is probably related to the production of smaller particles (and/or secondary particles generation; Table 2, C1 and C3–C5). The smaller the particles, the higher were the molecular weight of the resulting polymers. Polymerization reaction occurs in solution phase or particle phase swollen with monomer. Oxidant exists almost in the solution phase. In the latter case, therefore, the reactivity is considered to be dependent on the surface area of particles. Consequently, the molecular weight for smaller particles was higher because of the large surface area.

It is found that MMA–HEMA copolymer (30:70) unanimously afforded larger particles with a reasonable CV than PVP by the comparison of data in Tables 1 and 2. Normally, larger particle size is achieved by going through intensive nucleation and well-controlled coagulation of nuclei in the early stage of polymerization. As mentioned above, PVP forms the complex with the oxidant, $FeCl_3$, and deactivates it because of the coordination at higher concentration (20 wt%). At 10 wt%, the deactivation because of the complex formation seemed insignificant. Indeed, no big difference was observed between the molecular weight of products obtained with PVP and MMA–HEMA copolymer (30:70, 10 wt%). This result indicated that the polymerization rates in both cases were comparable each other. Therefore, the experimental result can not be kinetically explained. It is considered that the inherent characteristics of MMA–HEMA copolymers such as adsorption ability for oligomers and the solvating power in the reaction medium resulted in the intensive nucleation and well-controlled coagulation of nuclei in the early stage of polymerization. Higher stabilizing power of MMA–HEMA copolymer is suggested by the fact that more than 10 wt% PVP is necessary to stabilize the dispersion of particles in the experimental condition we examined, whereas in the case of MMA–HEMA copolymer, a stable dispersion was obtained even at 5 wt%. The alternative explanation is that the lower molecular weight nature of MMA–HEMA copolymer afforded the larger particles. It is previously reported for the dispersion polymerization of styrene in polar solvents that the increase of molecular weight of PVP used as stabilizer decreased the average particle diameter [24].

Conclusion

We successfully prepared the photoconductive microspheres by chemical oxidative dispersion polymerization of BTPA. The surface morphology was dependent on the polymerization temperature. At lower temperature (40 °C), porous particles were obtained with PVP as a dispersant. The utilization of statistical copolymer of MMA with HEMA (30:70) afforded particles with the narrowest distribution. The effort for improving monodispersity is still in progress. We will report the application of particles array consisting of photoconductive monodispersed particles in the near future.

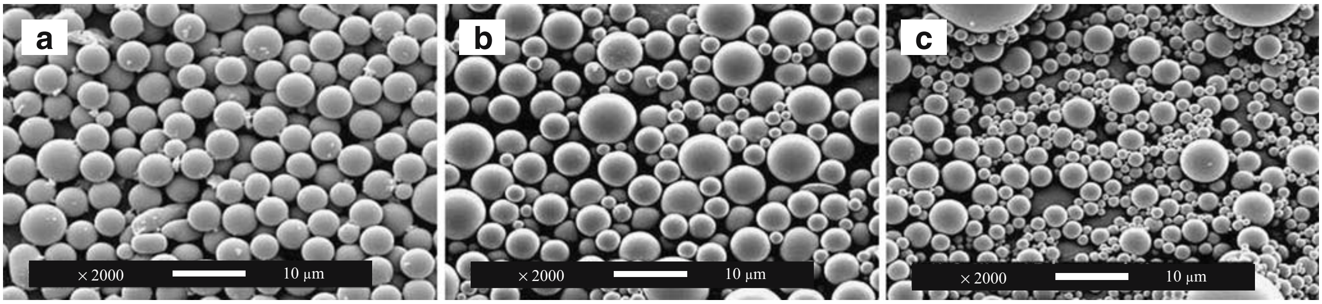

Fig. 3 SEM photographs of PBTPA particles prepared by chemical oxidative dispersion polymerization with different dispersant concentration. Dispersant, MMA/HEMA (3:7) concentration: 5 wt% (**a**), 10wt% (**b**), 15 wt% (**c**)

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