DISPERSION COPOLYMERIZATION OF STYRENE AND N-VINYL CARBAZOLE IN POLAR SOLVENTS

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ABSTRACT

Copolymer microspheres consisting of styrene and *N*-vinyl carbazole (NVC) have been prepared by dispersion polymerization. The effects of various polymerization parameters on the particle size were systematically studied. The particle size increased with the decrease of the system's initial solubility parameter and stabilizer concentration. When a small amount of inhibitor was added into the system, the particle size notably increased and the particle size distribution widened. The ratio of styrene to NVC in the monomer mixture had no obvious effect on particle size. The amount of NVC in the copolymers increases with the increase of NVC in the monomers.

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INTRODUCTION

Micron-size monodispersed polymer microspheres have been used in a wide variety of fields such as standard calibration, biomedical and clinical examinations, HPLC fillers, catalyst carriers, coating and ink additives, information storage materials [1-3].

Several techniques used for the preparation of monodispersed micron-size beads have been developed. Vanderhoff *et al*. [4] used successive seeding method to obtain micron-size monodispersed polymer particles. The particles with similar size were also prepared by Ugelstad *et al*. [5] by two-step swelling method. However, both approaches were tedious and typically required several reaction steps.

Dispersion polymerization is a very attractive method to prepare micron-size monodispersed polymer particles due to the inherent simplicity of its single-step process. It is quite suitable for the preparation of beads with the diameter range of 1-15 µm [6-10]. Preparation of micron-size monodispersed homopolymer particles has been extensively studied, especially polystyrene (PS) system and poly (methyl methacrylate) (PMMA) system [6-10]. Because dispersion polymerization is highly sensitive to small changes in the numerous reaction parameters involved in the process, the behavior of the polymerization may change when another monomer exists in the reaction medium, even the different comonomer ratio should be treated as a new polymerization parameter system. In 1987, Ober and Lok [11] prepared large monodispersed copolymer particles of styrene and n-butyl methacrylate by unseeded batch dispersion copolymerization in ethanol/water. Further study on this system was carried out by Frechet [12] *et al*. Recently, the dispersion polymerization systems of styrene/butyl acrylate and styrene/glycidyl methacrylate in polar solvents were also studied in detail [13-15].

The unseeded batch dispersion copolymerization of styrene and *N*-vinyl carbazole in ethanol/water (ethanol/toluene) medium was employed to prepare micron-sized monodispersed copolymer microspheres to achieve photoconductivity, and the influences of various polymerization parameters, such as the system's initial solubility parameter, stabilizer concentration, the composition of the monomer mixture and inhibitor concentration, on the particle size were studied systematically.

EXPERIMENTAL

Materials

Styrene (St) was purified by distilling under reduced pressure before polymerization. *N*-vinyl carbazole (NVC) was obtained from Aldrich Chemical Co. 2,2-Azobisisobutyronitrile (AIBN) was purified by recrystallization in ethanol. Polyvinylpyrolidone (PVP, Mw = 360,000) was supplied from BASF corporation. Deionized water was used throughout this work. Ethanol (EtOH), toluene and 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy (TEMPOL) were used as received.

Preparation of Copolymer Microspheres by Dispersion Copolymerization

In a typical example, 1.0 g PVP was dissolved in the mixture of 78 g ethanol and 2 g toluene in a 250 mL four-necked round-bottomed flask equipped with a mechanical stirrer, thermometer, reflux condenser, and nitrogen gas inlet and outlet. Then, a solution of 0.4 g AIBN in a mixture of 18 g styrene and 2 g NVC was added under stirring. The system was immersed in an oil bath, then the temperature of the mechanically stirred solution was raised to 70°C. Under a nitrogen atmosphere, polymerization was carried out at 70°C for 24 hours. After centrifugal purification the microspheres were dispersed into ethanol/water (v/v=3:1) for use.

Characterization of the Particles

Morphology analysis was carried out on a Hitachi S-520 Scanning Electron Microscopic (SEM). The particle size and size distribution were measured on a Coulter LS230. The compositions of the St/NVC copolymers were measured and calculated with Shimadzu UV-240 spectrophotometer. The dichloromethane was used as solvent and reference. The molecular weights of the copolymers were analyzed with Shimadzu LC-3A liquid chromatography in chloroform solutions at the detector wavelengh of 254 nm. A calibration curve was constructed with linear St standard. Tgs were determined on a Setaram DSC-92 differential scanning calorimeter under nitrogen at a heating rate of 10°C/min. FTIR spectra were recorded on a Magna 550 spectrophotometer, using KBr pellets.

RESULTS AND DISCUSSION

Dispersion polymerizations usually start in a homogeneous solution of monomer, a radical initiator, and a polymeric steric stabilizer in organic solvents, such as hydrocarbons or ethanol. First of all, polymerization in the solution formed oligomeric radicals. Because the reaction medium of dispersion polymerization does not dissolve the resultant polymer, the formed polymers precipitate and perhaps aggregate to form the colloidally unstable precursor particles (nuclei). These nuclei may further coalesce, and adsorb enough stabilizers from the medium onto their surface to become sterically stable. At this point, the total number of particles is fixed, and particle nucleation ceases. Subsequently, produced oligomers and precursors are captured by the existed particles before they can adsorb enough stabilizers to create a second generation of stable particles. This process of particle nucleation could be applied for all stabilizers, including graft copolymers formed *in situ*.

Effect of Initial Medium Polarity

The reaction medium of dispersion polymerization should be able to dissolve the steric stabilizer, but not to dissolve the resultant polymer. In dispersion polymerization, medium polarity plays a crucial role and influences the particle size and size distribution, because it controls the critical molecular weight, above which the polymer will precipitate. One method of estimating the polarity of a mixture of miscible liquids involves averaging the solubility parameter of the components. The solubility parameter, δ, is an empirical quantity that permits the calculation of a value representing the polarity of a solvent medium. The calculation of δ for a solvent mixture is done by taking the average based on the volume fraction of solvent in the mixture [16]. The average used in the calculations is given by

Where ϕ_i is the volume fraction of component i. Neither the polymeric stabilizer nor initiator is used in the estimation since they are only in small quantities. The polymer produced from the monomers is not included in the calculation since it locates in another separated phase. The solubility parameters of the individual components used in this study are summarized in Table 1 [17].

Table 2 shows the effect of the components in the solvent mixture on the solubility parameter of the system. The solubility parameter increased as the toluene content decreased and the water content increased. As shown in the Table 2 and Figure 1, when the solubility parameter increased, the particle size decreased. Because the polarity of copolymer P(St-NVC) is low, the critical mol-

TABLE 1. Solubility Parameter of Individual Components

Component	Solubility parameter $\delta_i (cal/cm^3)^{1/2}$
St	9.3
NVC	9.8*
Ethanol	12.7
Toluene	8.9
Water	23.4

*, calculated on the formula (dΣG/ M); G, the molar-attraction constant; ΣG is the sum for all the atoms and groups in molecules; d, the density; M, the molecular weight [17].

TABLE 2. Effect of Dispersion Medium on Particle Size and Size Distribution[a]

Sample	Medium (g/g)	$\bar{D}_v (\mu m)$[b]	CV(%)[c]	Init δ [d] $(cal/cm^3)^{1/2}$
R1	EtOH/H_2O 75/5	1.3	21	12.8
R2	EtOH/H_2O 78/2	1.5	16	12.4
R3	EtOH/H_2O 80/0	1.8	17	12.2
R4	EtOH/Toluene 78/2	1.8	14	12.1
R5	EtOH/Toluene 75/5	2.2	14	12.0
R6	EtOH/Toluene 70/10	7.6	71	11.8

a: 20%(w/w) monomers relative to total mixture, St/NVC(w/w) =18/2; 2% (w/w) AIBN relative to monomers; 5% (w/w) PVP relative to monomers.
b: Diameter is measured by Coulter LS230; $\bar{D}_v$ is volume-average diameter .
c: CV, the coefficient of variation of volume-average diameter.
d: Init δ , initial solubility parameter of system.
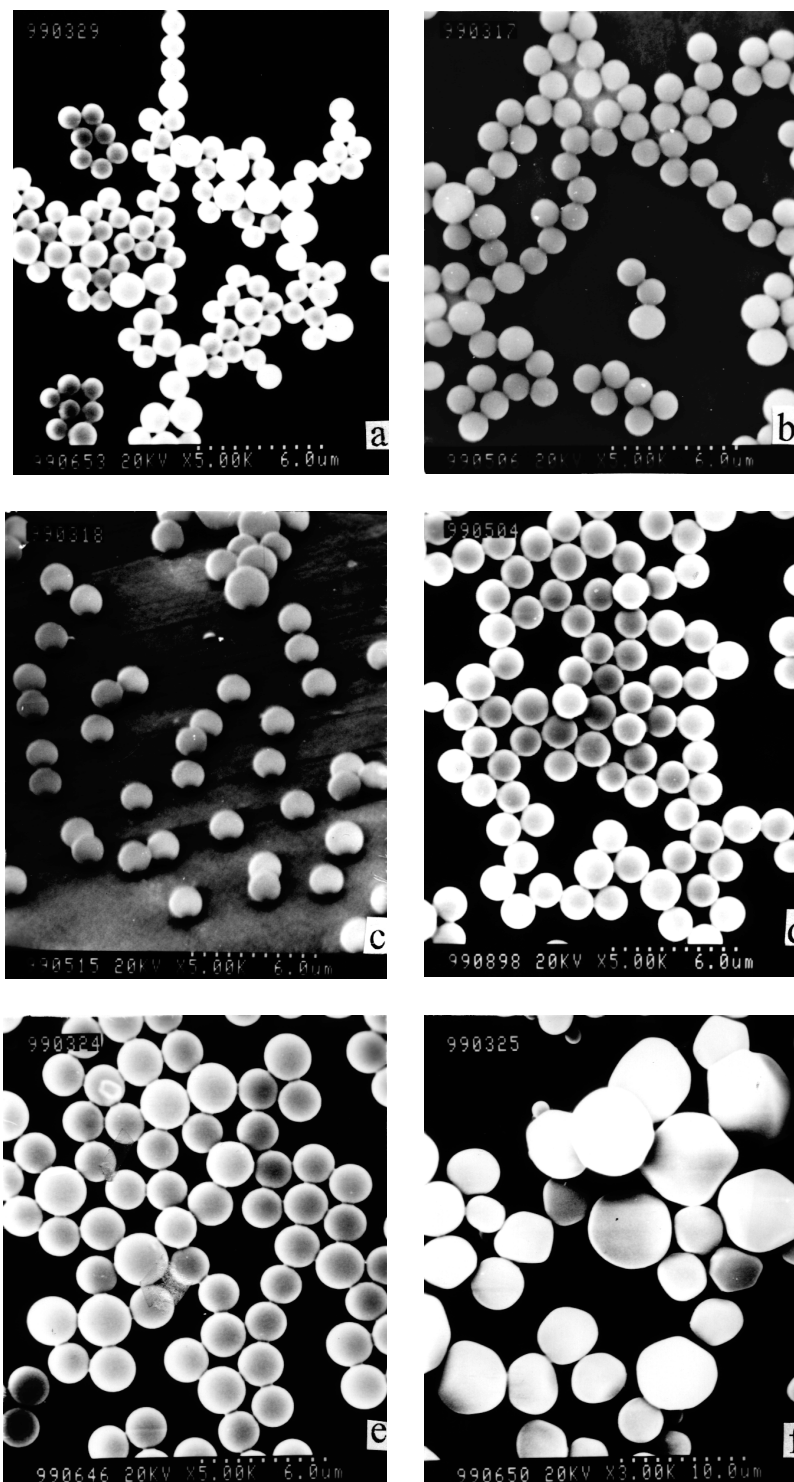
Figure 1. Effect of dispersion medium on particle size and size distribution: (a) R1; (b) R2; (c) R3; (d) R4; (e) R5; (f) R6.

TABLE 3.   Effect of Monomer Concentration on Particle Size and Size Distribution[a]

Sample	Monomer concentration[b](%)	$\bar{D}_v$ (μm)	CV(%)	Init δ $(cal/cm^3)^{1/2}$
R7	10	1.4	14	12.4
R8	15	1.5	13	12.2
R9	20	1.8	14	12.1
R10	25	1.8	14	12.0

a: St/NVC(w/w) =9/1; EtOH/Toluene(w/w)= 78/2; 2% (w/w) AIBN relative to monomers; 1.0g PVP.

b: monomer concentration relative to total mixture (w/w) .

TABLE 4.   Effect of Stabilizer Concentration on Particle Size and Size Distribution[a]

Sample	PVP concentration[b] (%)	$\bar{D}_v$ (μm)	CV(%)
R11	1	4.4	28
R12	3	2.0	16
R13	5	1.8	14
R14	7	1.7	12

a: EtOH/Toluene(w/w)= 78/2, 20%(w/w) monomers relative to total mixture, St/NVC(w/w)=18/2; 2% (w/w) AIBN relative to monomers.

b: PVP concentration relative to monomers (w/w).

ecular weight of copolymer decreases with the increasing of the polarity of system. Thus, by increasing δ, the critical chain length decreases and the rate of adsorbing the stabilizer-grafted copolymer onto the nuclei increases, then the smaller particles are obtained. For the R6, a broad particle size distribution was
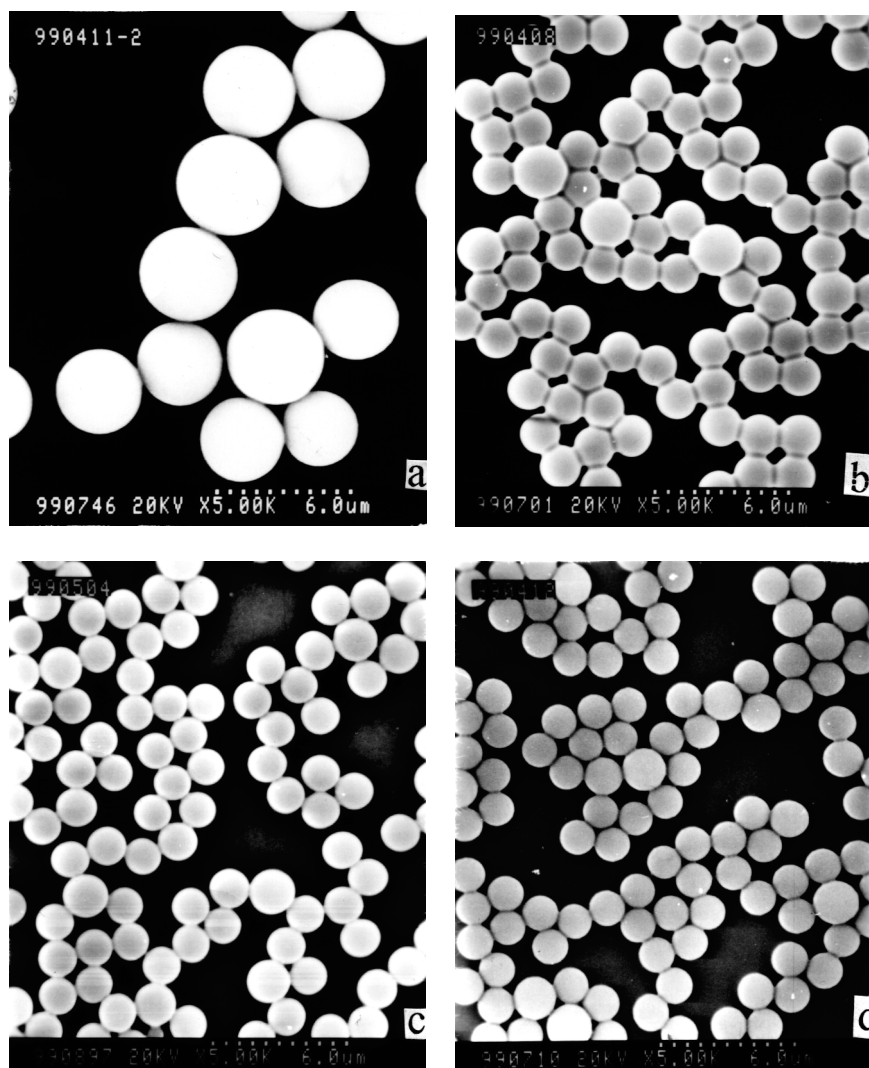
Figure 2. Effect of stabilizer concentration on particle size and size distribution: (a) R11; (b) R12; (c) R13; (d) 14.

obtained because its lower solubility parameter led to a longer nucleation stage. The reason about the formation of non-spherical particles (Figure 1.f), is still not clear.

With the increasing of the monomer concentration, the initial solubility parameter of system decreased, then the particle size slightly increased (Table 3), and the similar results were reported in references [7, 11, 12, 15]. The solubility

TABLE 5.   Effect of Inhibitor on Particle Size and Size Distribution[a]

Sample	inhibitor concentration [b] (%)	$\bar{D}_v$ (µm)	CV(%)
R15	0	1.8	14
R16	0.625	3.3	50
R17	1.25	5.4	56
R18	2.5	4.4	32

a: St/NVC(w/w) =9/1, 20%(w/w) monomers relative to total mixture;

EtOH/Toluene(w/w)= 78/2; 2% (w/w) AIBN relative to monomers; 1.0g PVP.

b: The inhibitor is 4-hydroxy-2,2,6,6- tetramethyl-piperidinyloxy (TEMPOL); inhibitor

concentration relative to AIBN (w/w).

parameter of both monomers is much lower than that of ethanol, therefore, the higher proportion of monomers will result in the lower average solubility parameter, and then will increase the critical chain length. Thus larger beads were obtained at higher monomer concentration.

Stabilizer Concentration

The stabilizer plays an important role in the preparation of narrow sized distribution particles produced by dispersion polymerization [7, 8, 12, 15]. From Table 4 and Figure 2, it can be found that the particle size decreased with the increase of the concentration of PVP stabilizer and reached a limit value finally. An increase in the concentration of PVP increases the viscosity of the medium and the rate of physical adsorption of PVP, as well as the rate of adsorption of the grafted stabilizer, since the amount of grafted stabilizer increases. All these would reduce the extent of aggregation of the nuclei and reduce the particle size. The particle size distribution became narrow with the increase of the concentration of PVP. In the higher PVP concentration system, the stage of the formation of stable particle became shorter, thus reduced the nucleation time, then a narrow sized distribution sample was obtained.
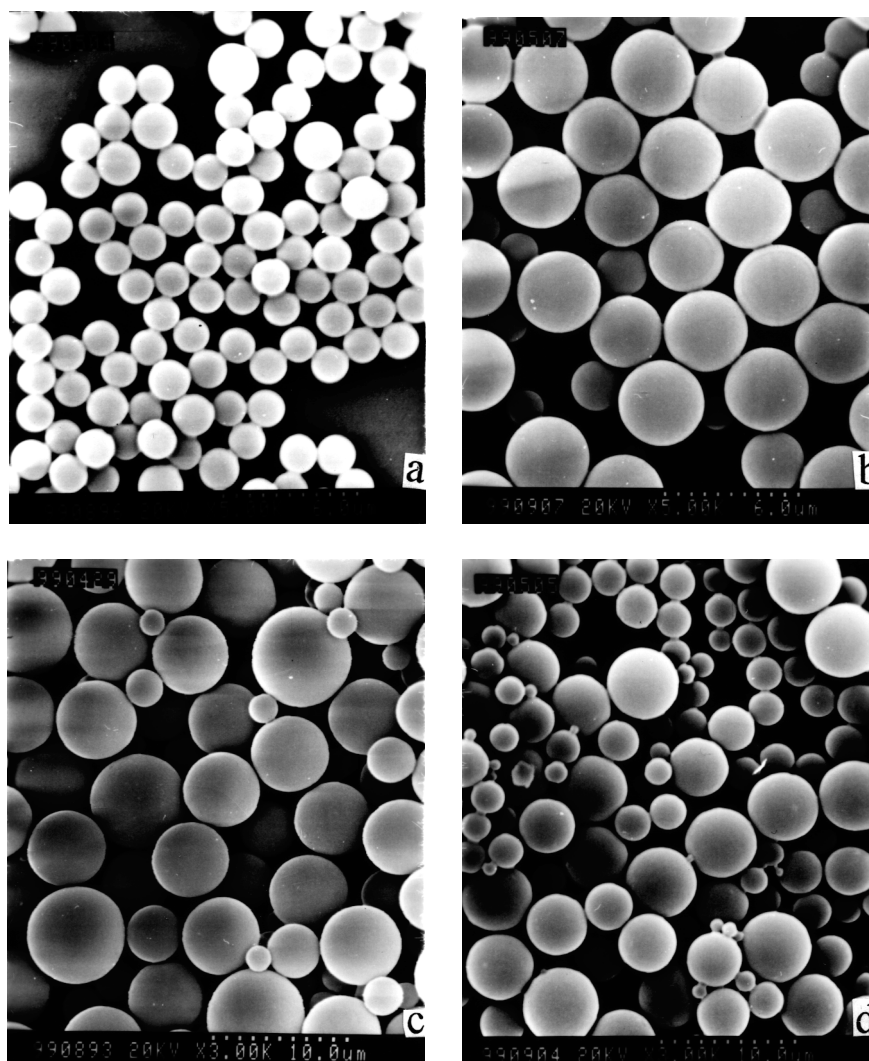
Figure 3. Effect of inhibitor concentration on particle size and size distribution: (a) R15; (b) R16; (c) R17; (d) R18.

Stabilizer Concentration

As seen in Table 5 and Figure 3, when a small amount of inhibitor, such as TEMPOL was added into the system, the particle size notably increased and the particle size distribution became broad. Because the inhibitor reduced the effective initiator concentration, and the particle size decreased as the initiator concentration decreased [7, 8, 10], this phenomenon can not be explained by the effective initiator concentration. We thought the reason may be as below: In nor-

TABLE 6.   Effect of Monomer Component on Particle Size and Size Distribution[a]

Sample	St/NVC(g/g)	$\bar{D}_v$ (μm)	CV(%)
R19	20/0	2.0	15
R20	19/1	1.9	15
R21	18/2	1.8	14
R22	17/3	1.9	17
R23	15/5	2.0	15

a: 20%(w/w) monomers relative to total mixture; EtOH/Toluene(w/w)= 78/8; 2% (w/w) AIBN relative to monomers; 5% (w/w) PVP relative to monomers, initial solubility parameter is $12.1(cal/cm^3)^{1/2}$.

mal process, the reaction system underwent a temperature rise process, and the nucleation stage (translucent) generally started when the temperature was below 70°C (such as 62°C). When a small amount of inhibitor was added in, the inhibitor would trap the initial free radical and then delay the polymerization reaction. Thus, the nucleation stage (translucent) actually took place at 70°C, and lead to the larger particles than that staring at the lower temperature [7, 8, 14]. At the same time, the existence of inhibitor would prolong the nucleation stage, thus resulting in broad particle size distribution.

Effect of Styrene/*N*-Vinyl Carbazole Ratio

Effect of St/NVC ratio on the particle size is shown in Table 6 and Figure 4. When the amount of the NVC in the monomer mixture changed, the particle size was hardly affected. Because the polarity and hydrophilicity of PVK are near to that of PS, the critical chain length of the copolymer richer in PVK may be close to that rich in PS, thus the particle size wouldn't change when the ratio of St/NVC changed.

Figure 5 shows the FTIR spectra of a styrene homopolymer R19 and a series P(St/NVC), R20~R23. PS has no absorption signal at 1624 cm^{-1}, or 1640 cm^{-1}, and the copolymers have those absorption peaks, which can be assigned to
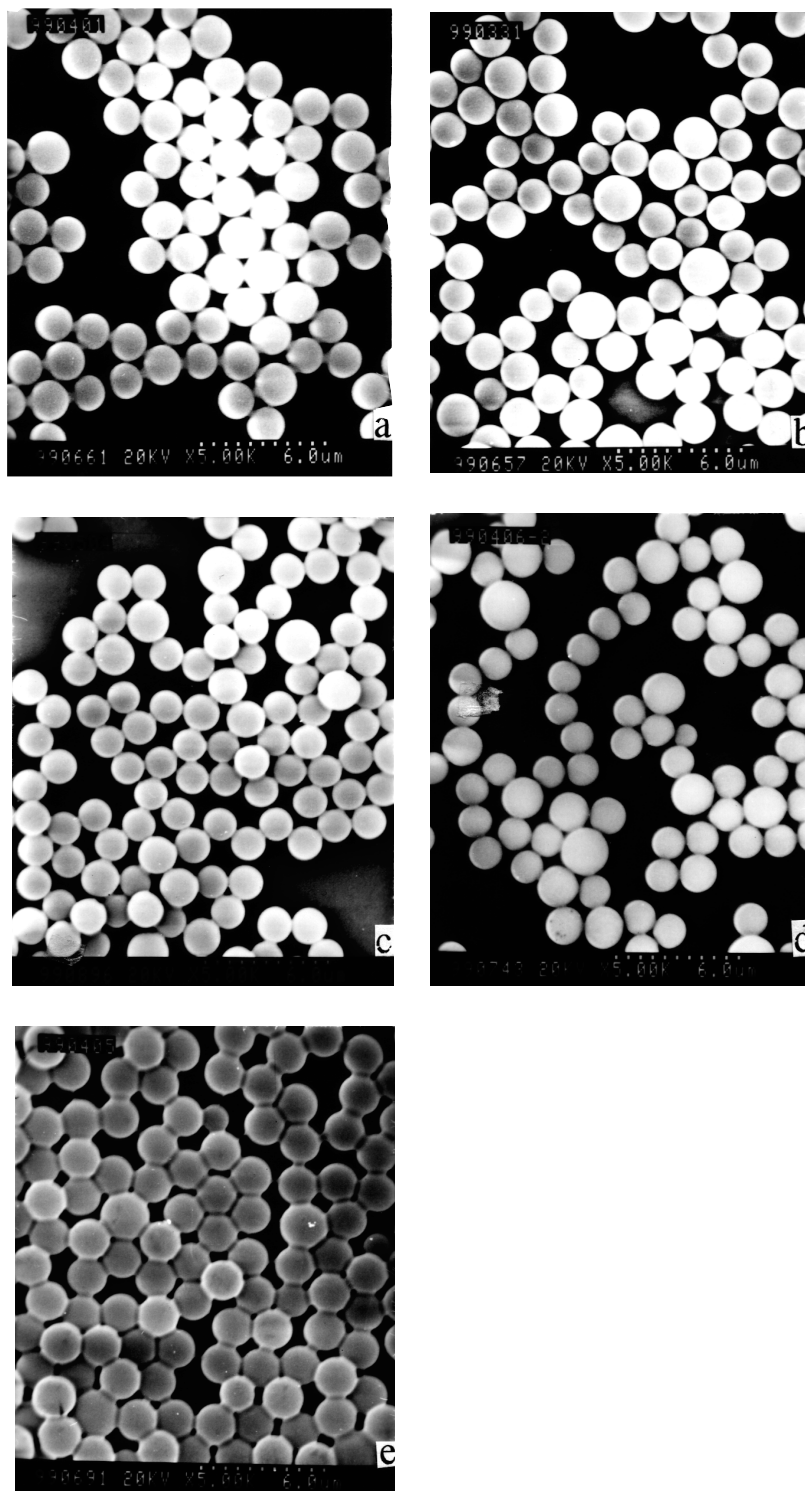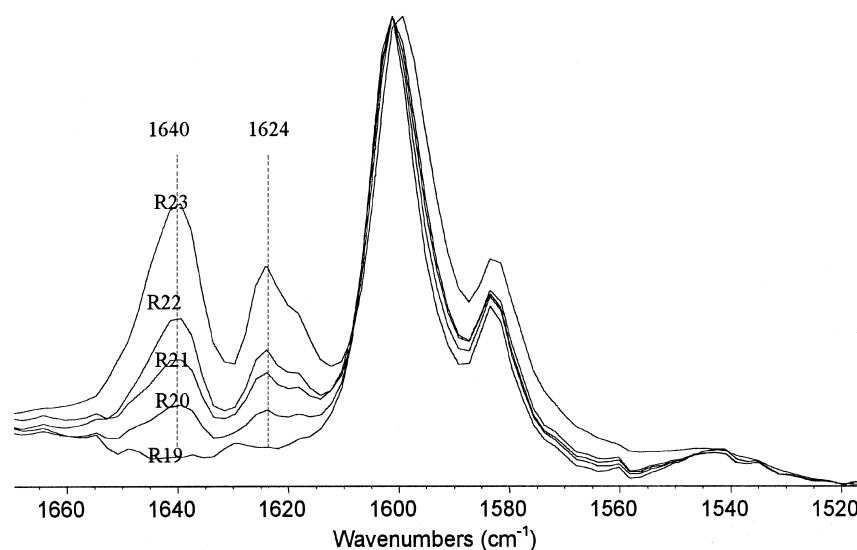
Figure 4.   Effect of monomer component on particle size and size distribution: (a) R19; (b) R20; (c) R21; (d) R22; (e) R23.

Figure 5. FTIR spectra of the copolymers: R19; R20; R21; R22; R23.

the vibration of the carbon-nitrogen of the PVK [18]. From R20 to R23, the heights of these absorption peaks increased, which indicated the amount of PVK in the copolymers increases with the increase of NVC in the monomers.

Figure 6 shows the UV-Vis absorption spectra of pure PS, PVK and the copolymer P(St/NVC), R21. There is no absorption band above 300 nm for PS, but PVK has two absorption peaks above 300 nm, and one of them is 340 nm. The absorption spectrum of R21 is similar to that of PVK. We choose 340 nm as the work wavelength, and by changing the concentration of PVK in the dichloromethane, we measure the absorption intensity of a series PVK solution. Then, the plot of the amount of PVK vs the peak intensity at 340 nm was drawn. By measuring the peak height of the copolymers, the amount of PVK in the copolymers were calculated and listed in Table 7. The amount of PVK was increased from 0% (R19) to 20.4% (R23). By comparing the amount of PVK in the copolymers with that of NVC in feed monomers, we found relatively low PVK contents in copolymer. This is because of the different reactivity ratios of styrene (monomer 1) and NVC (monomer 2)($r_1>1$, $r_2<1$) [19].

DSC measurements showed that the increase in PVK amount in the copolymer increases the Tg (Table V7). The molecular weights and molecular weight distribution of the polymers (R19-R23), are also described in Table 7.
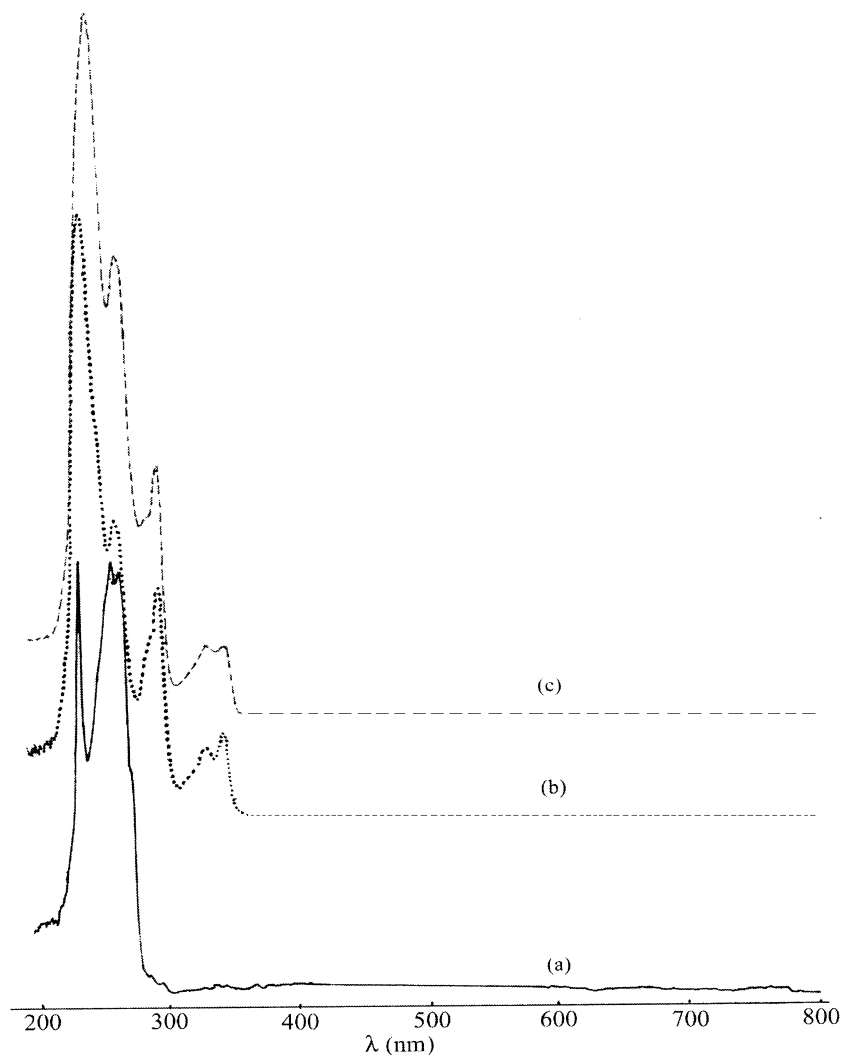
Figure 6.   UV-Vis spectra of: (a) PS; (b) PVK; (c) R21, P(St/NVC) microspheres.

They generally had low molecular weight and broad molecular weight distribution, similar to those in solution polymerization.

CONCLUSION

The dispersion polymerization of styrene and *N*-vinyl carbazole in ethanol-water (toluene) medium was studied in a batch reactor. The effects of

TABLE 7.   Characterization of the Copolymers with Different Monomer Components

Sample	NVC in monomers(%)	PVK in copolymer(%)[a]	Tg(℃)	Mn ($\times 10^3$)	Mw ($\times 10^3$)	Mw/Mn
R19	0	0	98.0	8.6	32	3.7
R20	5	4.0	99.7	14	35	2.5
R21	10	7.6	102.8	21	21	3.7
R22	15	11.4	103.8	29	29	2.4
R23	25	20.4	105.5	27	27	2.3

a: Calculated on UV-Vis, work wavelength is 340nm, and the dichloromethane was used as solvent and reference.

various polymerization parameters on the particle size were systematically studied. The particle size increased with the decrease in the system's initial solubility parameter and stabilizer concentration. When a little inhibitor was added into the system, the particle size notably increased and the particle size distribution widened. The ratio of styrene to *N*-vinyl carbazole in the monomer mixture has no obvious effect on the particle size. FTIR, UV-Vis spectra and DSC measurements indicate that the amount of poly(N-vinyl carbazole) in the copolymers increases as the amount of NVC in the monomers increased.

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