High T_g Microspheres by Dispersion Copolymerization of N-Phenylmaleimide with Styrenic or Alkyl Vinyl Ether Monomers

SWAPNA KRISHNAMOORTHY, MEHUL HARIA, BLYTHE E. FORTIER-McGILL, M. A. JAFAR MAZUMDER, ERICA I. ROBINSON, YAN XIA, NICHOLAS A. D. BURKE, HARALD D. H. STÖVER

Department of Chemistry and Chemical Biology, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4M1

ABSTRACT: Solution and dispersion copolymerizations of N-phenylmaleimide (PMI) with either styrenics or alkyl vinyl ethers (AVEs), systems with a tendency to give alternating polymers, were investigated with the goal of producing high glass transition particles. Equimolar solution copolymerization of PMI with styrenics gave alternating copolymers, whereas AVEs gave PMI-rich copolymers (~65:35) except for t-butyl vinyl ether, which gave copolymers with only a slight excess of PMI. These copolymers had glass transition temperatures (T_gs) ranging from 115 to 225 °C depending on comonomer(s). Dispersion copolymerization in ethanol-based solvents in the presence of poly(vinylpyrrolidone) as steric stabilizer led to narrow-disperse microspheres for many copolymers studied. Dispersion copolymeriations of PMI with styrenics required good cosolvents such as acetonitrile or methyl ethyl ketone as plasticizers during particle initiation and growth. Dispersion copolymerizations generally resulted in copolymer particles with compositions and T_gs very similar to those of the corresponding copolymers formed by solution polymerization, with the exception of t-butyl vinyl ether (tBVE), which now behaved like the other AVEs. Dispersion terpolymerizations of PMI (50 mol %) with different ratios of either n-butylstyrene and t-butylstyrene or n-butyl vinyl ether and tBVE led to polymer particles with T_gs that depended on the ratio of the two butyl monomers. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 192–202, 2011

KEYWORDS: copolymerization; dispersions; glass transition; high T_g microspheres; polymer particles

INTRODUCTION

Monodisperse polymer microspheres are being developed for use as coating materials in a variety of applications. Besides emulsion-type processes used to prepare high volume latex particles, dispersion polymerizations in nonaqueous media are commonly used to prepare larger microspheres of several micron diameter.[1–5]

Most dispersion polymer microspheres are based on styrenic and acrylic polymers, and accordingly have a glass transition temperature (T_g) around 100–140 °C or below. It is known that the incorporation of maleimides into styrenic or acrylic polymers results in elevated T_g and in improved resistance to thermal degradation. For instance, the 50:50 copolymer of styrene and N-phenylmaleimide (PMI) has a T_g of ~230 °C[6–8] and an onset of thermal degradation at ~340 °C,[6,7] compared with 100 °C[9] and 273 °C,[7] respectively, for polystyrene. Koning and coworkers[8] studied a series of styrene-maleimide copolymers made with different N-substituted maleimides. The T_g values of the 50:50 copolymers were much higher than that of polystyrene, but were not simply related to the relative sizes of the N-substituents: H (252 °C); Me (205 °C); tBu (178 °C); Ph (221 °C); 4-tBuPh (237 °C); and 4-PhOPh (194 °C). In spite of the promising thermal properties of copolymers containing maleimides such as PMI, little work has been directed toward the preparation of well-defined, high T_g polymer particles[10] composed of these materials. Semibatch emulsion copolymerization of maleimides with styrene has been reported to give sub-100 nm copolymer particles.[11]

The basic parameters controlling nonaqueous dispersion polymerization were determined several years ago by the groups of Lok and coworkers,[12–14] Paine and coworkers,[15–21] El-Aasser and coworkers,[1,22,23] and others.[24–26] Solid particles nucleated by the phase separation of forming polymer are colloidally stabilized by surface capture of an added steric stabilizer such as poly(vinylpyrrolidone) (PVP) or methyl cellulose. In fact, graft copolymers of the stabilizer formed during polymerization are thought to be the key species involved in stabilization of the particles. The solvency of the reaction medium determines whether polymerization occurs predominantly in the solution or in the particle phase, and it further affects the solubility of the graft copolymer stabilizers that control particle nucleation and stabilization.
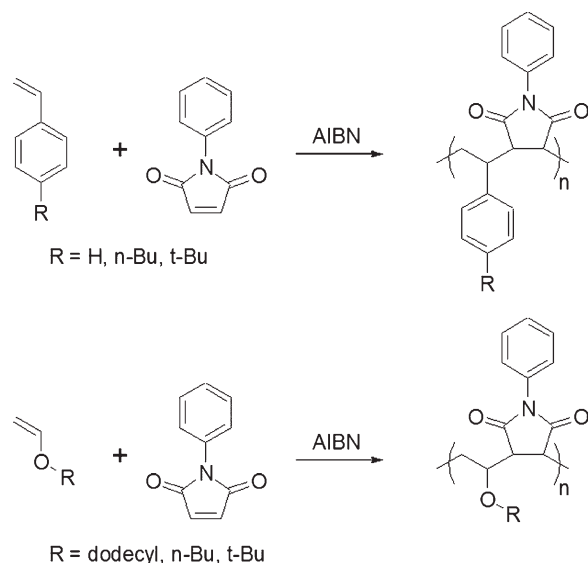
SCHEME 1 Styrene—phenylmaleimide and AVE—phenylmaleimide copolymers.

Importantly, in ethanol or alkanes, the solvents most commonly used for dispersion polymerization of styrene and alkyl methacrylates, the T_g of the forming polymers are suppressed below the reaction temperature of $\sim$70 °C, permitting these graft copolymers to remain at the surface of the microspheres, and not become trapped below the surface of the growing particles.[20] Formation of dispersion polymer particles based on inherently higher T_g polymers may, hence, hinge on finding solvents that similarly plasticize the particles and allow the steric stabilizer to remain at the surface of the growing particle.

The work described in this article employed PVP as steric stabilizer and explores the role of solvent composition, monomer loading, and stabilizer loading on the morphology, size, and yield of dispersion copolymer particles formed from PMI with different comonomers: styrene (S), 4-*t*-butylstyrene (tBS), 4-*n*-butylstyrene (nBS), *n*-butyl vinyl ether (nBVE), *t*-butyl vinyl ether (tBVE), and *n*-dodecyl vinyl ether (DDVE; Scheme 1). These materials should have high and tunable T_g values and may find applications as high T_g coatings and binders. In addition, solution polymerizations were carried out to prepare control samples for T_g measurements.

EXPERIMENTAL

Materials

nBVE (98%), tBVE (98%), DDVE (98%), S (99%), tBS (93%), PMI (97%), and PVP [special grade, molecular weight = 40 kDa] were purchased from Aldrich (Oakville, ON), and used as received. Methyl ethyl ketone (MEK, Reagent grade), heptane (Reagent), methanol (MeOH, Reagent), *N*,*N*-dimethylformamide (DMF, Reagent), dioxane (Reagent), ethyl ether (Reagent), tetrahydrofuran (THF, HPLC grade), and acetonitrile (AN, HPLC) from Caledon Laboratories (Georgetown, ON) were used as received. Ethanol (EtOH, Commercial Alcohols, Brampton, ON) was used as received. Azobis(isobutyroni-

trile) (AIBN) was received as a gift from DuPont Canada and used as received. nBS was prepared by a modified version of the literature procedure[27,28] as described in the Supporting Information.

Solution Polymerization

Solution polymerizations were typically carried out at 10% (w/v) monomer loading with 1 mol % AIBN relative to monomers in dioxane, THF, or DMF. For example, nBVE (1.832 g; 18.3 mmol), PMI (3.168 g; 18.3 mmol), AIBN (0.060 g; 0.36 mmol), and THF (45 mL) were placed in a 60 mL polyethylene screw cap bottle. The mixture was heated from room temperature to 60 °C in 1 h and then maintained at 60 °C for 24 h in an oven equipped with a set of horizontal rollers that rotate the bottle(s) at $\sim$4 rpm. The copolymer, p(nBVE-*co*-PMI), was isolated by precipitation in MeOH (500 mL), washed with MeOH, and then dried to a constant weight in a vacuum oven at 60 °C. Yield: 3.08 g (62%).

Dispersion Polymerization

Typical dispersion polymerizations of S, nBS, or tBS with PMI were carried out at 2% monomer loading with 1 wt % AIBN and 16 wt % PVP relative to the monomers. Typical dispersion polymerizations of alkyl vinyl ethers (AVEs) and PMI were carried out at 2% monomer loading with 2 wt % AIBN and 8 wt % PVP relative to the monomers. For example, S (0.751 g; 7.2 mmol), PMI (1.249 g; 7.2 mmol), PVP (0.320 g), AIBN (0.020 g), and a 30:70 (vol %) mixture of AN/EtOH (100 mL) were placed in a 125 mL polyethylene screw cap bottle. The bottle was placed in the oven and rotated (4 rpm), while being heated from room temperature to 60 °C in 1 h and then maintained at 60 °C for 24 h. After the reaction was complete, the polymer particles were isolated and cleaned by centrifugation and redispersal (3X) in EtOH. The particles were dried to a constant weight in a vacuum oven at 60 °C. Yield: 1.66 g (83%).

Characterization

Particles were examined using an Olympus BH-2 optical microscope including an attached digital still camera, and with a Phillips Electroscan 2020 environmental scanning electron microscope (ESEM) operating in SEM mode. Dry samples were sputter coated with a thin layer of gold ($\sim$10 nm) before ESEM analysis. Average molecular weights were determined by size exclusion chromatography (SEC) on a Waters SEC system consisting of a Waters 515 HPLC pump, Waters 717 plus Autosampler, three Waters Styragel columns (HR2, HR3, and HR4; 30 cm × 7.8 mm; 5 μm particles), and a Waters 2414 refractive index detector. THF (1.0 mL/min) was used as the eluent and the system was calibrated with narrow-disperse polystyrene standards.

Differential scanning calorimetry (DSC) was carried out with a TA Instruments DSC 2910 calibrated with indium. Samples were heated at 10 °C/min and T_g was taken as the midpoint of the transition during the second heating cycle. Particle sizes were determined in two ways: (1) by measuring $\sim$100 individual diameters from ESEM images using UTHSCSA ImageTool software and (2) with a 256-channel Coulter Multisizer II for particles suspended in an electrolyte solution

TABLE 1 Composition and T_gs of Copolymers of PMI with S, nBS, tBS, nBVE, tBVE, or DDVE[a]

Comonomer	Feed Ratio (M:PMI)	Composition (mol % M:PMI)[b]	T_g (°C)	Predicted T_g (°C)[c]
S[d]	50:50	50:50	223	215
nBS	50:50	50:50	167	150
nBS + tBS	25:25:50	27:23:50	193	176
tBS	50:50	50:50	226 ± 3[e]	212
tBVE	50:50	47:53	201	216
nBVE[f]	96:4	47:53	141	103
nBVE	50:50	37:63	174	142
DDVE	50:50	35:65	116	(96)[g]

[a] Prepared by solution polymerization in THF or dioxane unless otherwise indicated.
[b] Measured by ^{1}H NMR.
[c] T_g predicted with Fox equation.[38]
[d] Sample made by dispersion polymerization in MEK/EtOH (35:65).
[e] Average for four samples, two made by solution polymerization in dioxane and two by dispersion polymerization in AN/EtOH (10:90).
[f] Sample made in neat nBVE.
[g] Measured T_g for 50:50 copolymer.[34]

(Isoton II). The aperture used in the Coulter Multisizer limits the particles measured to those with d > 1 μm. As many of the samples had a significant fraction of particles with d < 1 μm, the data from the Coulter Multisizer is reported as the diameter at the peak of the size distribution curve.

^{1}H NMR spectra were measured in CDCl$_3$ or CD$_2$Cl$_2$ solution on a Bruker AV-200 (200 MHz). The compositions of copolymers of PMI with S, nBS, tBS, nBVE, tBVE, or DDVE were determined from the NMR spectra by comparison of the area of the phenyl peaks at 6.2–7.6 ppm with the area of the signals due to the backbone H-atoms, the *t*-butyl peak at 1.2 ppm (tBS and tBVE), and/or the methyl signal at 0.9 ppm (nBS, nBVE, and DDVE).

RESULTS AND DISCUSSION

The project was aimed at developing microspheres with T_gs in excess of 150 °C that were easily controlled by: (a) selection of appropriate monomer pairs, (b) varying copolymer composition, or (c) preparing terpolymers of PMI (50 mol %) with mixtures of two styrenic or two vinyl ether monomers (50 mol % total).

There are few prior studies of dispersion polymerization directed toward copolymers,[14,22,29,30] due, in part, to the need to deal with complications arising from (a) the effect of reactivity ratios on copolymer compositions, (b) the possible differential partitioning of the monomers between the particle and solution phases known as the Harwood–Bootstrap effect, and (c) possible interference by the comonomer(s) with particle nucleation. These issues could lead to drifts in copolymer compositions that would result in core-shell gradients in copolymer composition in cases where there is little mixing within the growing polymer microspheres, and possibly to problems in maintaining colloidal stability. The work described here focuses on dispersion polymerizations carried out in polar solvents, with the assumption that the

preferred locus of polymerization is the continuous phase, rather than the particle phase. In addition, monomers with a tendency to form alternating copolymers were selected such that narrow composition ranges near 50:50 might be formed. To aid the understanding of these copolymerizations, a series of copolymers of PMI with S, nBS, tBS, DDVE, nBVE, or tBVE have been prepared by both solution and dispersion polymerizations.

Solution Copolymerization of PMI with Styrenics and AVEs

The compositions and T_g values of copolymers of PMI with S, nBS, tBS, nBVE, tBVE, or DDVE prepared by solution polymerization are shown in Table 1. The copolymers of PMI with S, nBS, or tBS showed comonomer ratios close to a 1:1 ratio, consistent with the known tendency of S/PMI to form alternating polymers.[6–8,10,31–33] A poly(nBS-*co*-tBS-*co*-PMI) terpolymer was similarly found to have a composition with a 1:1 ratio of styrenics to PMI.

PMI also has a tendency for alternation with other electron-rich monomers such as AVEs,[34] although the reactivity ratios for nBVE (0) and PMI (0.35) suggest that PMI will be preferentially incorporated into these copolymers,[35] as observed previously in other maleimide/vinyl ether systems.[36] Indeed, copolymerization of PMI with nBVE or DDVE gave polymers enriched in PMI, but interestingly for tBVE-PMI, the incorporation was nearly 50:50 (Table 1). Kharas and Ajbani[37] have observed similar behavior for the copolymerization of tBVE with other electron-poor monomers, which was attributed to preferential formation of charge transfer complexes by tBVE, because it adopts an s-*trans* conformation about its C—O bond, unlike other AVEs.

The supporting information includes additional compositional information on a series of poly(nBVE-*co*-PMI) copolymers and poly(nBVE/tBVE-*co*-PMI) terpolymers prepared by

solution polymerization (Supporting Information Fig. S1 and S2).

Thermal Properties of Copolymers

The T_g values for copolymers made with a 1:1 molar feed ratio of PMI and various comonomers are shown in Table 1 along with the actual polymer composition as measured by NMR. The T_g value for a poly(nBVE-co-PMI) copolymer with a composition close to 50:50 made by using excess nBVE during polymerization is included as well. Also shown in Table 1 are T_g values predicted by the Fox equation,[38] using the known T_g values of PS (100 °C), PtBS (~130 °C), PnBVE (−55 °C), and PtBVE (88 °C),[9] and an estimated T_g (325 °C) for PPMI.[7] For PnBS, values of 6 °C[9] and 48 °C[39] have been reported and the higher value was used to give the predicted T_g shown in Table 1. PtBS and PnBS samples made in this work were found to have T_g values of 124 and 18 °C, respectively, in reasonable agreement with values found in the literature.

A poly(S-co-PMI) sample made by dispersion polymerization in MEK/EtOH (35:65) gave $T_g = 223$ °C, within the range of values (215–235 °C) reported in the literature for poly(S-co-PMI) of approximately 50:50 composition.[6–8,10] Several poly (tBS-co-PMI) samples were made by both solution and dispersion polymerization and showed an average $T_g = 226 \pm 3$ °C, similar to the value observed for poly(S-co-PMI). Although the T_g for PtBS, the homopolymer of tBS, is higher than that of PS (~130 °C vs. 100 °C),[9] the weight fraction of the high T_g component (PMI) in a 50 mol % copolymer is lower in poly(tBS-co-PMI).

As expected, poly(nBS-co-PMI) had a lower T_g than poly(S-co-PMI), 167 versus 223 °C, and the poly(nBS-co-tBS-co-PMI) terpolymer made with a 25:25:50 feed ratio had a T_g value (193 °C) roughly halfway between those of poly(nBS-co-PMI) (167 °C) and poly(tBS-co-PMI) (226 °C). Thus, it should be possible to control T_g within this range by varying the nBS:tBS ratio in the terpolymer. The T_g of 116 °C measured for the poly(DDVE-co-PMI) copolymer with 65 mol % PMI content is consistent with the value of 96 °C measured for a 50:50 copolymer by Kohli et al.[34]

For copolymers with roughly 50 mol % PMI, T_g ranges from approximately 100–225 °C in the order DDVE < nBVE < nBS < tBVE < S = tBS. Although the Fox equation reproduces the overall trend in T_g values, the measured and predicted values differ by approximately 10–15 °C in most cases and by >30 °C for the nBVE copolymers. This may be due, in part, to uncertainty in T_g for PPMI or PnBVE and to the tendency of these systems to form alternating rather than random copolymers as well as to limits in the use of the symmetric Fox equation.[40]

Figure 1 compares the T_g of poly(nBVE-co-PMI) prepared by both solution and dispersion polymerization. Overall, the T_g of the copolymers increases from approximately 140–220 °C as PMI content rises from 50 to 80 mol %. The T_g values for polymers prepared by dispersion polymerization were typically lower than those of similar composition prepared by solution polymerization. This is likely due to the lower
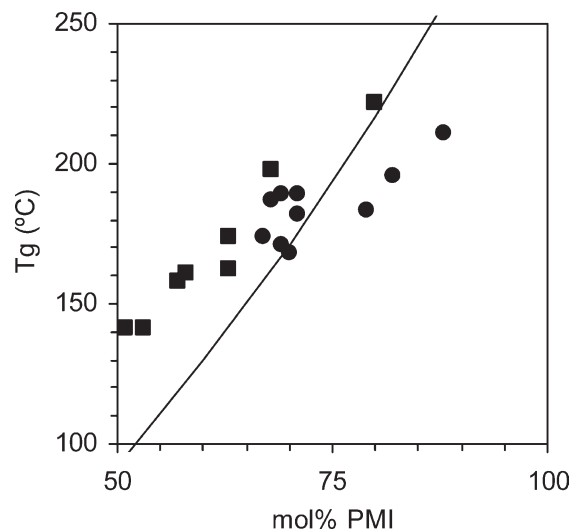

FIGURE 1 T_g versus PMI content for poly(nBVE-co-PMI) prepared by solution (■) and dispersion (●) polymerization. The line represents T_g as predicted by the Fox equation.

molecular weights produced in the dispersion polymerizations, which typically employed lower monomer loadings and higher initiator/monomer ratios than solution polymerizations. For example, poly(nBVE-co-PMI) copolymers containing 68–69 mol % PMI prepared by solution and dispersion polymerization showed molecular weights (M_n) of 8300 and 2400 g/mol, respectively. Although the values measured by PS-calibrated SEC may underestimate the true molecular weight, they showed a consistent trend of lower molecular weight for copolymers made by dispersion polymerization.

Also shown in Figure 1 is a curve of predicted T_g based on the Fox equation. It lies close to the values measured for the poly(nBVE-co-PMI) copolymers but exhibits a steeper slope. As mentioned, this discrepancy may be related to the uncertainty in T_g for the PPMI and PnBVE, the alternating nature of these copolymers, or the low molecular weight of high PMI-content polymers.

Another approach used to control T_g was to polymerize PMI with mixtures of nBVE and tBVE. For a fixed PMI content, terpolymer T_g should fall as higher nBVE to tBVE ratios are used. Indeed, for polymers made with a 50 mol % PMI feed, T_g decreased steadily from 201 to 174 °C as more nBVE was used (Fig. 2). The decrease is not as pronounced as might have been expected, if the PMI content had remained constant across the series (dashed line in Fig. 2). The less efficient copolymerization of nBVE compared with tBVE leads to lower total AVE-content in the polymers and to preferential incorporation of tBVE relative to nBVE (Supporting Information Fig. S2). Thus, the lower T_g expected as nBVE replaces tBVE in the feed is partly offset by increased PMI and tBVE content in the polymers relative to nBVE.

Hence, high T_g polymers have been successfully prepared by polymerization of PMI with S, nBS, tBS, nBVE, or tBVE, and it was demonstrated that T_g may be controlled by monomer selection or by varying the composition of copolymers or
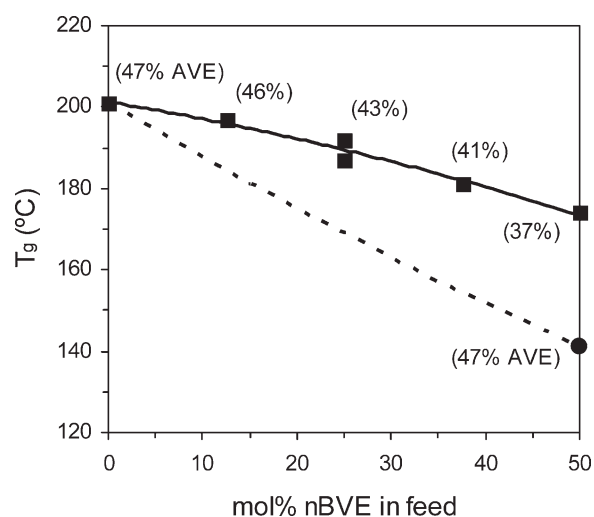
FIGURE 2 T_g versus fraction of nBVE relative to tBVE in the feed for poly(nBVE-co-tBVE-co-PMI) terpolymers prepared by solution polymerization. The total AVE content of each copolymer is indicated in brackets. Data point for poly(nBVE-co-PMI) containing 47% nBVE (●) and predicted T_g for terpolymers containing 47 mol % AVE (dashed line) are shown.

terpolymers. The following sections describe preparation of microspheres by dispersion polymerization of these copolymer and terpolymer systems.

Conditions for Dispersion Polymerization

The reaction medium is a key element in determining the success of dispersion polymerization and the size of the particles produced. Qualitative observations of the solubility of poly(S-co-PMI) and poly(nBVE-co-PMI) in several solvents are given in Table 2, along with the solubility parameters for those solvents.[41] The poly(S-co-PMI) copolymer is soluble or swollen in solvents of intermediate polarity and intermediate H-bonding ability. The Hansen solubility parameters for poly(S-co-PMI) (50:50), calculated by the method of van Krevelen,[42] were found to be $\delta_t = 18.6$; $\delta_d = 17.3$; $\delta_p = 2.8$;

and $\delta_h = 6.1$ MPa$^{1/2}$. The solubility of this copolymer in THF and chloroform, solvents with δ_p and δ_h values similar to those calculated for the copolymer, supports this estimate.

In this work, dispersion polymerizations of PMI with S, nBS, and tBS were conducted in binary mixtures of EtOH, a non-solvent for the copolymers, together with either MEK or AN. Dispersion polymerizations of poly(DDVE-co-PMI), poly(nBVE-co-PMI), and poly(tBVE-co-PMI) were carried out in EtOH or MeOH or in mixtures of EtOH with MEK, heptane, MeOH, or water.

The effects of both stabilizer and monomer loading on the dispersion polymerization of the poly(S-co-PMI) system were investigated. At a constant total monomer loading of 2% (w/v) in a 30:70 (v/v) mixture of AN:EtOH, a solvent that gave narrow-dispersed microspheres (vide infra), the particle diameter decreased (Supporting Information Fig. S3) with PVP loading as expected.[15,18,22,26] The polymer molecular weight remained constant (22 ± 1 kDa) as PVP loading was varied, as it is determined largely by monomer loading and the monomer to initiator ratio. A small amount of coagulum was formed at lower PVP levels (<16 wt % relative to monomer or 3.2 g/L), but significant particle yield (59% vs. 22% coagulum) was observed at PVP levels as low as 0.8 wt % (0.16 g/L), much below the levels commonly used in dispersion polymerizations.

The effects of monomer loading on particle properties were investigated for poly(S-co-PMI) by varying monomer loading from 1 to 10% (w/v) at a constant 8 wt % PVP loading relative to monomer. The polymer yield increased (from 66 to 97%) with increased monomer loading. It is interesting to note that the yield is high even at 1% monomer loading, which likely reflects the high reactivity of this donor–acceptor pair of monomers. The particle size and polymer molecular weight were found to increase with monomer loading (Supporting Information Fig. S3). The particle diameter increased from 1.43 to 1.78 μm as the monomer loading was increased from 2 to 10%, implying that particle number does not increase as rapidly as monomer loading, an effect that has

TABLE 2 Solubility of Poly(S-co-PMI) and Poly(nBVE-co-PMI) in Various Solvents and Solubility Parameters for Those Solvents

| Solvent | Solubility at 20 (°C)/60 (°C)[a] | | Solubility Parameters[b] | | | |
	Poly(S-co-PMI)	Poly(nBVE-co-PMI)[c]	δ_t (Mpa$^{1/2}$)	δ_d (Mpa$^{1/2}$)	δ_p (Mpa$^{1/2}$)	δ_h (Mpa$^{1/2}$)
MeOH	i/i	i/–	29.7	15.1	12.3	22.3
EtOH	i/i	i/sw	26.6	15.8	8.8	19.4
AN	sw/s	s/s	24.6	15.3	18	6.1
THF	s/s	s/s	19.4	16.8	5.7	8
MEK	sw/s	s/s	19	16	9	5.1
Chloroform	s/s	s/s	19	17.8	3.1	5.7
Heptane	–	i/i	15.3	15.3	0	0

s, soluble; i, insoluble; sw, swollen.
[a] Polymer (1 wt %).
[b] Ref. 41.
[c] Poly(nBVE-co-PMI) Containing 67 mol % PMI.

TABLE 3 The Effect of Monomer Loading on Poly(nBVE-*co*-PMI) Particle Properties[a]

Loading (wt %)	Yield (%)	nBVE[b] (%)	M_n (kg/mol)[c]	T_g (°C)
2	34	21	2.6	183
4	67	31	4.7	189
6	77	32	5.8	187
8	85	29	4.3	189
10	81	29	4.5	182

[a] Polymerization conditions: nBVE:PMI = 30:70 (mol %); MEK/EtOH 20:80 (vol %); 2 wt % AIBN, and 8 wt % PVP; 60 °C/24 h.
[b] Measured by ^{1}H NMR.
[c] Measured by SEC in THF.

been observed in other studies and was ascribed to improved solvency with increased monomer loading.[12,14,15,22,24]

The effect of monomer loading was also explored for the poly(nBVE-*co*-PMI) system (Table 3). Dispersion polymerization of a 30:70 mixture of nBVE/PMI was conducted with a constant PVP loading of 8 wt % relative to monomer in a 20:80 (v/v) mixture of MEK:EtOH, conditions that gave spherical particles. When the monomer loading was greater than 2%, the particle yield, nBVE content, and polymer molecular weight were significantly higher (Table 3). The molecular weights as measured by SEC calibrated with PS standards seem quite low, but they likely underestimate the true polymer molecular weight. The low nBVE content of the particles made at 2% monomer loading could result from an incomplete polymerization that favors PMI incorporation or to partial phase separation favoring PMI-rich polymer chains. Despite the higher PMI content, the polymer formed at 2% monomer loading had a similar T_g to the other samples, perhaps because of its lower molecular weight.

The effects of the solvent composition used during dispersion polymerization on particle morphology and size are described in the following sections. The experiments were conducted at low monomer loading (2%) to minimize effects of monomer on solvency. In addition, low PVP loading (8–16 wt % relative to monomer) was used to minimize its incorporation into the final material and any effect on T_g.

Dispersion Polymerization of PMI with AVEs
Poly(DDVE-*co*-PMI)
The poly(DDVE-*co*-PMI) [35:65] obtained from a 50:50 mol % feed was found to be soluble or swollen in a wide range of solvents, and it proved difficult to find a suitable solvent for dispersion copolymerization of these two monomers. Dispersion polymerization was attempted in EtOH or EtOH containing MEK (10–30 vol %), heptane (10–25%), MeOH (10%), or water (5%), but in all cases, it resulted in low yields (8–40%) of spherical particles with a broad size distribution (0.5–5 μm, Supporting Information Fig. S4). The polymerization solutions were either clear or only slightly turbid at 60 °C; however, they became increasingly cloudy on cooling to room temperature. Apparently, poly(DDVE-*co*-PMI) and its graft copolymer with PVP are fairly soluble in

these solvents at 60 °C, but less so at room temperature, and a thermally induced phase separation occurs resulting in spherical particles with a broad size distribution. The low yield of particles is likely due to incomplete phase separation of the poly(DDVE-*co*-PMI) copolymer on cooling. Solvents with reduced solvency for poly(DDVE-*co*-PMI), such as water or heptane, were not explored because of the limited solubility of the PMI monomer.

Poly(nBVE-*co*-PMI)
The poly(nBVE-*co*-PMI) [35:65] copolymer was less soluble in EtOH than poly(DDVE-*co*-PMI), and, thus, a better candidate for dispersion polymerization. Typical dispersion polymerizations were carried out with a 1:1 mol ratio nBVE/PMI at 2% total monomer loading in neat EtOH or in EtOH containing MEK, AN, or heptane, and gave particle yields ranging from 34% in AN:EtOH = 10:90 (vol %), a better solvent for the copolymer, to 69% in heptane:EtOH = 25:75, a poorer solvent. The particles from each polymerization contained approximately 30–33 mol % nBVE, similar to that observed in solution polymerizations.

Figure 3 displays ESEM images of the poly(nBVE-*co*-PMI) particles formed in several different solvents. In neat ethanol, narrow-disperse microspheres were obtained (2.3 ± 0.2 μm diameter), but some coagulation is evident in the ESEM image [Fig. 3(d)]. Addition of 10% AN to the polymerization solvent led to polymer that was soluble at 60 °C but underwent partial precipitation at room temperature as observed with poly(DDVE-*co*-PMI). The addition of 15–25 vol % MEK led to formation of very small, plasticized particles that appeared to aggregate on work up [Fig. 3(f)]. Polymerization in the presence of 10 or 20 vol % heptane gave particles similar to those formed in neat EtOH [Fig. 3(b,c)], whereas addition of 25 vol % or more heptane led to a range of particle sizes and included rough, irregularly shaped particles [Fig. 3(a)].

The production of flattened or misshapen particles indicates that significant plasticization occurred during polymerization. The use of still poorer solvents to suppress this plasticization and consequent deformation was hindered by the limited solubility of the PMI monomer. Instead, experiments were done in which the PMI content of the copolymers was increased to reduce plasticization by (a) reducing polymer solubility in EtOH and (b) increasing copolymer T_g. Dispersion polymerization of nBVE and PMI in EtOH at 2% monomer loading with feeds containing 60, 70, 80, and 90 mol % PMI resulted in particles that do not show signs of deformation because of overplasticization (Fig. 4). In fact, the opposite problem, lack of plasticization, is probably occurring for particles made with 80 and 90% PMI [Fig. 4(c,d)], where irregular or rough particles are formed. The particles contained 69, 79, 82, and 88 mol % PMI, and had T_g values of 171, 183, 196, and 211 °C, respectively. With increasing PMI content in the feed, the yield of particles dropped from ~50% for 50:50 and 40:60 feed ratios to ~30% for 30:70, 20:80, and 10:90 feed ratios. The particles formed at 60 and 70% PMI feeds are spherical with a narrow size range, 2.6 ± 0.3 and 3.6 ± 0.5 μm, respectively [Fig. 4(a,b)]. Thus, it is
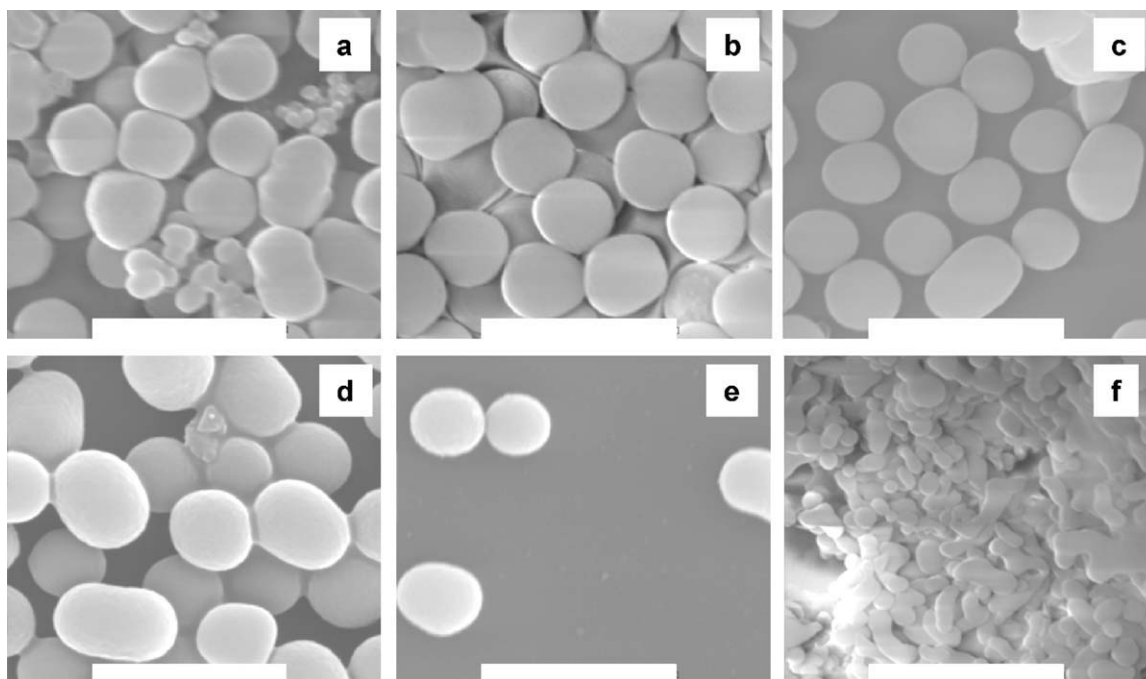
FIGURE 3 ESEM images of poly(nBVE-*co*-PMI) particles prepared by dispersion polymerization in various solvents: (a) EtOH/heptane (75:25 vol %); (b) EtOH/heptane (80:20); (c) EtOH/heptane (90:10); (d) EtOH; (e) EtOH/MEK (90:10); and (f) EtOH/MEK (75:25). Experimental conditions: nBVE:PMI 50:50 (feed); 2% monomer loading; 8 wt % PVP relative to monomers; 2 wt % AIBN relative to monomers; and 60 °C/24 h. Size bars = 5 μm.

possible to prepare narrow-disperse high T_g particles (170–180 °C) by dispersion copolymerization of nBVE with PMI.

Poly(tBVE-co-PMI) and Poly(nBVE-co-tBVE-co-PMI)

Dispersion polymerization of PMI with tBVE or tBVE/nBVE mixtures was examined, as these copolymers had high and readily tuned T_g values (~140–200 °C; Fig. 2). Dispersion polymerization of a 50:50 mixture of tBVE/PMI in EtOH gave particles that settled and stuck to the walls of the vessel during polymerization, were polydisperse and contained some precipitated material. The polymer formed during the dispersion polymerization was insoluble in acetone, AN, or THF and showed limited solubility in chloroform, dichloromethane, DMF, or dimethylsulfoxide. ^{1}H NMR analysis of the polymer in CDCl$_3$ showed that the polymer contained significantly more PMI than the copolymer made with the same feed ratio by solution polymerization in dioxane (65% vs. 53 mol %, Table 4).

When the PMI feed was decreased to 40 or 30 mol %, colloidally stable dispersions were obtained following polymerization. The copolymers were readily soluble in chloroform and were determined to contain 59 and 53 mol % PMI, respectively, by ^{1}H NMR analysis. The compositions of poly(tBVE-*co*-PMI) formed by dispersion polymerization in EtOH are similar to those seen for poly(nBVE-*co*-PMI) formed by either solution (Supporting Information Fig. S1) or dispersion polymerization. The reduced reactivity of tBVE, to a level comparable with that of nBVE, is also seen during the formation of poly(nBVE-*co*-tBVE-*co*-PMI) terpolymers by dispersion polymerization (Table 4).

Thus, it appears that tBVE behaves differently under dispersion polymerization conditions in EtOH than during solution copolymerization in dioxane. As described earlier, it is
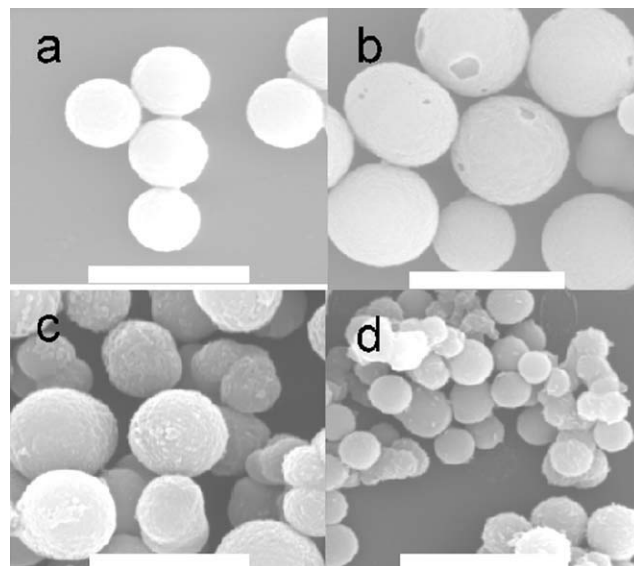

FIGURE 4 ESEM images of poly(nBVE-*co*-PMI) particles prepared by dispersion polymerization in EtOH at different monomer feed ratios: (a) 40:60; (b) 30:70; (c) 20:80; and (d) 10:90. Experimental conditions: 2% monomer loading; 8 wt % PVP relative to monomers; 2 wt % AIBN relative to monomers; and 60 °C/24 h. Size bars = 5 μm.

TABLE 4 Compositions of Poly(nBVE-*co*-tBVE-*co*-PMI) Made by Dispersion or Solution Polymerization

Comonomer Feed	nBVE:tBVE:PMI	
	Solution Polymerization	Dispersion Polymerization
50:0:50	37:0:63	37:0:63
0:50:50	0:47:53	0:35:65
25:25:50	18:25:57	17:17:66
35:35:30	–	22:22:56

believed that charge-transfer complexes are involved in solution polymerizations of tBVE with electron-poor monomers. In more polar solvents such as ethanol, the formation of charge-transfer complexes may be reduced or eliminated with the result that tBVE behaves more like nBVE during polymerization with PMI.

The above results indicate that dispersion copolymerization of AVEs with PMI is possible, given proper choice of cosolvents so as to avoid overplasticization and dissolution on one hand and under-plasticization on the other hand. The particles obtained have high T_g, but the drift in composition due to preferential incorporation of PMI narrows the T_g range achievable. Further studies will be needed to look into the formation of compositional gradients from core to surface of some of the microspheres formed.

### Dispersion Polymerization of PMI with Styrenics
Styrenic comonomers and PMI are expected to give stable compositions in dispersion copolymerization, given their pronounced tendency for alternating copolymerization.
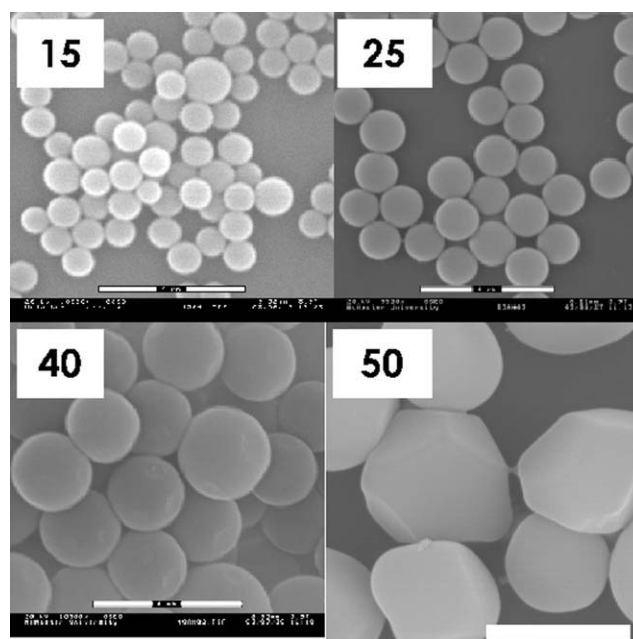
Poly(S-co-PMI)
The effect of solvency on the size and morphology of poly(S-*co*-PMI) particles was investigated using MEK/EtOH and AN/EtOH mixtures. In these experiments, the following conditions were kept constant: 2% (w/v) monomer loading, 1:1 mole ratio of S to PMI, 2% (w/w) AIBN relative to monomer, and the polymerizations were conducted at 60 °C for 24 h. The PVP loading was maintained at 3.2 g/L, or 16% relative to monomer, a loading that was found to provide suitable colloidal stabilization while minimizing the potential carryover of PVP into the particles. The dispersion polymerizations had typical yields of 70–80%, quite high considering the 2% monomer loading.

ESEM images of poly(S-*co*-PMI) particles prepared in various MEK/EtOH or AN/EtOH mixtures are shown in Figures 5 and 6, respectively. Pure EtOH or solvent mixtures with low levels of MEK (≤25 vol %) or AN (≤10 vol %) yielded rough, irregularly shaped particles as shown in Figure 5 for particles prepared in 25 vol % MEK. Presumably, the fine particles (nuclei) formed initially by phase separation are insufficiently plasticized under these conditions to allow coalescence of the precipitated polymer into spherical particles.

As the MEK or AN levels were increased, narrow-disperse microspheres were formed, and the diameter increased with
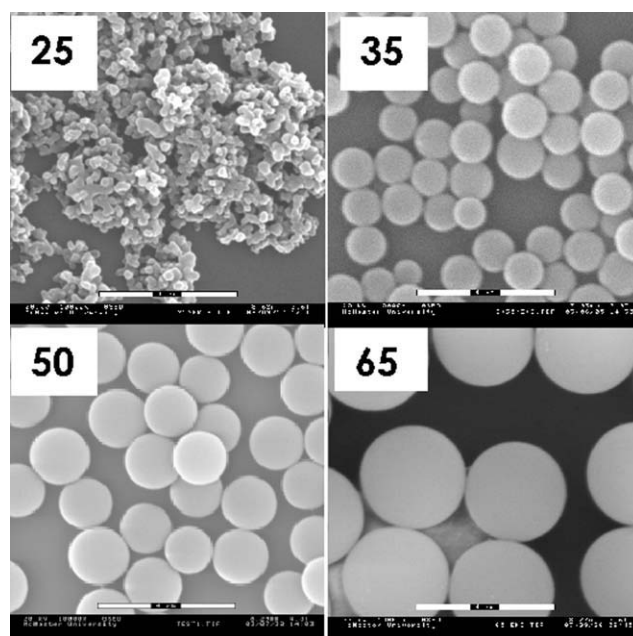
FIGURE 5 ESEM images of poly(S-*co*-PMI) particles prepared in 25, 35, 50, and 65 vol % MEK in EtOH. Experimental conditions: S:PMI 50:50 (feed); 2% monomer loading; 16 wt % PVP relative to monomers; 1 wt % AIBN relative to monomers; and 60 °C/ 24h. Size bars = 4 μm.

MEK or AN levels, as shown in Figure 5 for particles prepared in 35, 50, and 65 vol % MEK or Figure 6 for particles prepared in 15, 25, 40, and 50 vol % AN. When even higher

FIGURE 6 ESEM images of poly(S-*co*-PMI) particles prepared in 15, 25, 40, and 50 vol % AN in EtOH. Experimental conditions: S:PMI 50:50 (feed); 2% monomer loading; 16 wt % PVP relative to monomers; 1 wt % AIBN relative to monomers; and 60 °C/24 h. Size bars = 4 μm.
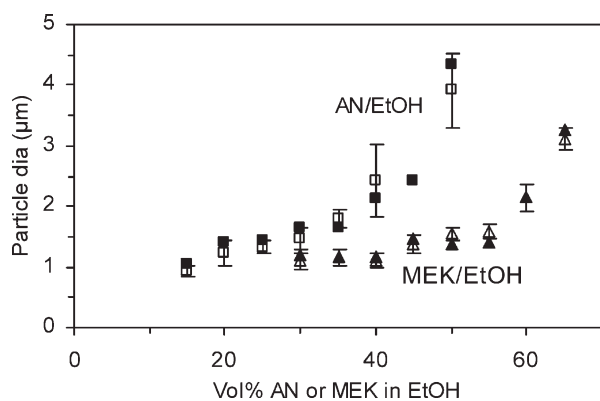
FIGURE 7 Particle diameter versus MEK or AN content of reaction solvent for poly(S-*co*-PMI) particles prepared in (△, ▲) MEK/EtOH or (□, ■) AN/EtOH. Diameters from ESEM images (open symbols) or the peak of the Coulter Multisizer curve (closed symbols). Error bars show standard deviation of ESEM measurement.

MEK or AN levels were used, considerable amounts of soluble polymer was present at the end of the polymerizations, although some broadly dispersed microspheres would separate from solution on cooling the reaction mixture in some cases. The particles formed at 50% AN deformed visibly on drying, suggesting that they were highly plasticized or swollen by the reaction medium. The particles formed in AN/EtOH mixtures are larger than those formed in MEK/EtOH mixtures of the same composition, and lower AN content is required for the onset of microsphere formation (15% AN vs. 30% MEK). This indicates that AN is a better solvent than MEK for the poly(S-*co*-PMI) copolymer and the PVP-*graft*-poly(S-*co*-PMI) stabilizer.

Figure 7 summarizes the effect of solvent composition on particle diameter measured by ESEM and with a Coulter Multisizer II. Diameters measured with the two techniques show good agreement. The particle diameters increase steadily as the solvency improves as observed previously in the dispersion polymerization of styrene,[12–15,17,22,24] and consistent with the mechanism developed by Paine.[16] In the early stages of polymerization, particle nuclei are formed by polymer precipitation and begin to coalesce into larger particles. At the same time, some of the PVP is grafted with poly(S-*co*-PMI) and is incorporated into the growing particles. Once the particles have sufficient stabilizer on their surfaces, they are protected from coalescence with other similar-sized particles. If stabilization occurs early, a large number of small particles will result, whereas stabilization at a later stage will lead to fewer but larger particles. It is believed that solvent properties influence particle size primarily by affecting the solubility of the graft copolymer. In solvents with lower MEK or AN content, the poly(S-*co*-PMI) segments of the graft copolymer are insoluble and will be efficiently adsorbed by the particles, whereas the PVP blocks are fully solvated. This leads to earlier stabilization and, hence, numerous and smaller particles. With increasing MEK or AN content, the poly(S-*co*-PMI) grafts become more soluble, fewer stabilizer

chains are adsorbed onto the particles, and, hence, larger particles are formed. Ultimately, the increasing solubility of the base polymer prevents particle formation, and the system reverts to a solution polymerization.

The polar and H-bonding solvent parameters for a number of solvents are shown in Figure 8. The area within this solvency map in which spherical particles were observed is marked with an oval. The lines joining EtOH with either AN or MEK represent the δ_p and δ_h values for mixtures of the two pure solvents estimated with $\delta(mix) = [f_A(\delta_A)^2 + f_B(\delta_B)^2]^{1/2}$, where δ_A is the solvent parameter for solvent A, and f_A is its volume fraction in the mixture. The calculated δ_p and δ_h values for PVP[43] and poly(S-*co*-PMI) were used to place points for these two polymers on Figure 8. Successful dispersion polymerization requires a solvent in which monomer and stabilizer readily dissolve but the polymer is insoluble and, thus, strongly H-bonding solvents such as MeOH or EtOH appear to be ideal solvents for the dispersion polymerization. However, the particles formed in these solvents were irregularly shaped, not spherical. Spherical particles were only obtained when MEK or AN was added to EtOH. Thus, there is the additional requirement that the polymerization solvent must be able to plasticize the solid polymer to allow particle coalescence, and to permit the stabilizer to remain near the particle surface during growth. The degree of plasticization required will be higher for polymers such as poly(S-*co*-PMI), where the polymerization temperature is 160 °C below T_g, than for polymers like PS, where the typical polymerization temperature is only 30–40 °C below T_g.

Within the set of solvents that gave spherical particles, the particle size was found to increase as the H-bonding strength of the solvent decreased, moving from right to left in the oval. Previous studies of PS dispersion polymerization found that the largest particles were obtained with the solvent that best matched the solubility properties of the stabilizer.[15,17] A
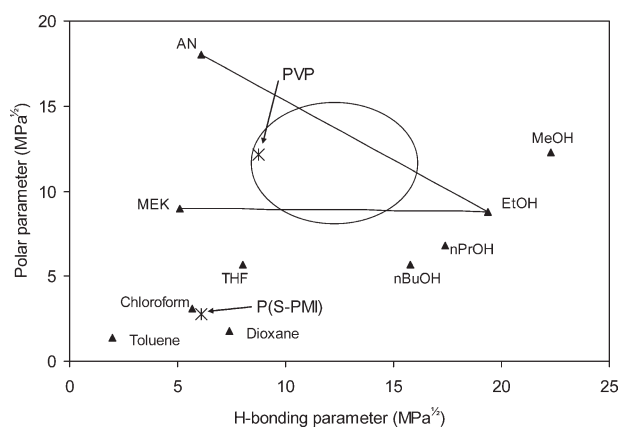

FIGURE 8 Solvent map for poly(S-*co*-PMI) polymerization plotted in terms of the polar and H-bonding Hansen solubility parameters. Area within the oval indicates MEK–EtOH and AN–EtOH mixtures in which narrow-disperse spherical particles were obtained by dispersion polymerization at 60 °C. Calculated values for PVP and poly(S-*co*-PMI) [50:50] are shown also.
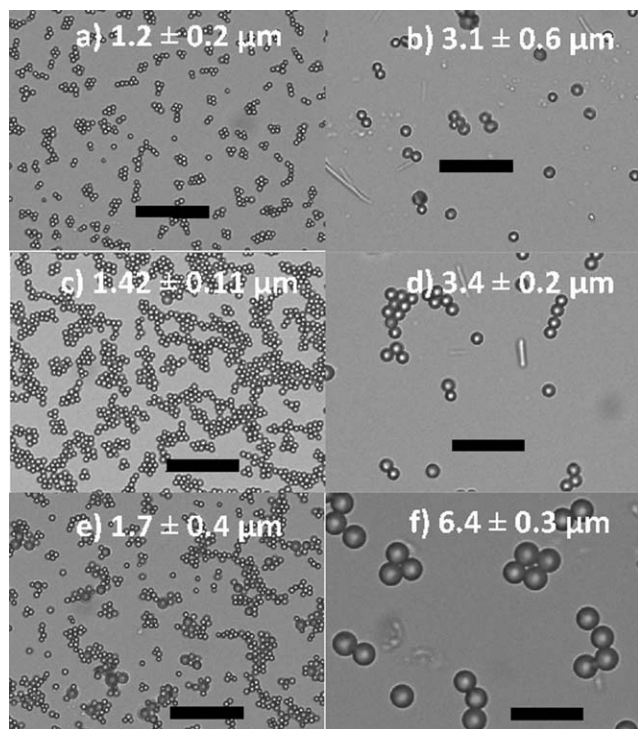
FIGURE 9 Optical microscope images (a,b) poly(nBS-PMI), (c,d) poly(nBS-tBS-PMI), and (e,f) poly(tBS-PMI) particles made in 9:1 EtOH/AN (left column) or 8:2 EtOH/AN (right column). Experimental conditions: (nBS+tBS):PMI 50:50 (feed); 2% monomer loading; 16 wt % PVP relative to monomers; 1 wt % AIBN relative to monomers; and 60 °C/24 h. Size bars: 20 μm.

similar trend is observed here with the largest particles produced in solvents that closely match the polar and H-bonding solubility parameters reported for PVP.[43]

Poly(nBS-co-PMI) and Poly(nBS-co-tBS-co-PMI)

Studies were extended to copolymers of PMI with nBS and/or tBS to allow access to particles with a T_g that could be varied in the range of approximately 150–225 °C. Dispersion polymerization of PMI with nBS and/or tBS was carried out using the same polymerization conditions as used for poly(S-co-PMI). The polymerization feed contained 50 mol % PMI and 50 mol % of the styrene component(s). As observed with poly(S-co-PMI), rough and irregular particles were formed for each of the polymers in neat EtOH indicating that the polymers were insufficiently plasticized to allow particle coalescence (images not shown). Addition of 10 vol % AN led to small spherical particles (Fig. 9).

Analysis of these particles by ^{1}H NMR revealed compositions identical to the feed compositions with 50 mol % PMI and 50 mol % of the styrenic component(s). The polymers formed in dispersion polymerization had molecular weights (M_n, 14–21 kDa) that were two to three times lower than for polymers made by solution polymerization, not surprising given the different monomer loadings (2 vs. 10%). Despite the lower molecular weight, the polymers formed by dispersion polymerization had high T_g values that were nearly

identical to those seen for copolymers made by solution polymerization: poly(nBS-co-PMI)—172 °C versus 167 °C; poly(tBS-co-PMI)—226 °C versus 225 ± 3 °C; poly(nBS-co-tBS-co-PMI)—195 °C versus 193 °C.

When the AN content of the solvent was increased to 20 vol % the particle size increased significantly as shown in Figure 9. The change from insufficiently plasticized, irregular particles to large spherical particles happens over a much narrower solvent range than was observed for the S-PMI system (Fig. 7), suggesting that AN must be a better solvent for copolymers of PMI with nBS and/or tBS than it is for S-PMI copolymers.

CONCLUSIONS

Dispersion polymerization of styrenic and AVE monomers with PMI has been shown to result in narrow disperse copolymer microspheres, provided the solvency of the reaction medium can be adjusted to strike a balance between several requirements: to dissolve the polar monomer PMI, to permit phase-separation of the forming copolymers at the temperature of polymerization, and to plasticize the growing polymer microspheres enough to permit the PVP-graft copolymer that functions as steric stabilizer to remain near the particle surface. In practice, these requirements can be met with solvent mixtures comprised of ethanol with small to moderate amounts of good cosolvents such as AN or MEK. Thus, it was possible to prepare narrow-disperse high T_g particles (170–180 °C) by dispersion copolymerization of nBVE with PMI. The copolymer particles formed from PMI and styrenic comonomers maintain a strict 50:50 comonomer ratio, facilitating the use of mixtures of styrene monomers such as nBS/tBS or nBS/S to tune the terpolymer T_g up to 225 °C. The resulting tunable high T_g microspheres may find applications as high temperature film formers.

REFERENCES AND NOTES

1 Shen, S.; Sudol, E. D.; El-Aasser, M. S. J Polym Sci Part A: Polym Chem 1994, 32, 1087–1100.

2 DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. Science 1994, 265, 356–359.

3 Croucher, M. D.; Winnik, M. A. In Scientific Methods for the Study of Polymer Colloids and Their Applications; Candau, F.; Ottewill, R. H., Eds.; Kluwer Academic: Dordrecht, 1990; pp 35–72.

4 Kawaguchi, S.; Ito, K. Adv Polym Sci 2005, 175, 299–328.

5 Song, J.-S.; Tronc, F.; Winnik, M. A. J Am Chem Soc 2004, 126, 6562–6563.

6 Barrales-Rienda, J. M.; Gonzalez de la Campa, J. I.; Gonzalez Ramos, J. J Macromol Sci 1977, A11, 267–286.

7 Liu, G.; Li, X.; Zhang, L.; Qu, X.; Liu, P.; Yang, L.; Gao, J. J Appl Polym Sci 2002, 83, 417–422.

8 Teerenstra, M. N.; Steeman, P. A. M.; Iwens, W.; Vandervelden, A.; Suwier, D. R.; Van Mele, B.; Koning, C. E. e-Polymers 2003, 045.

9 Andrews, R. J.; Grulke, E. A. In Polymer Handbook, 4th ed.; Brandrup, J.; Immergut, E. H; Grulke, E. A., Eds.; Wiley-Interscience: Toronto, 1999; pp VI/193–VI/277.

10 Yuan, Y.; Siegmann, A.; Narkis, M.; Bell, J. P. J Appl Polym Sci 1996, 61, 1049–1054.

11 Yuan, Y.; Siegmann, A.; Narkis, M.; Bell, J. P. Polym Adv Technol 1995, 6, 671–677.

12 Lok, K. P.; Ober, C. K. Can J Chem 1985, 63, 209–216.

13 Ober, C. K.; Lok, K. P.; Hair, M. L. J Polym Sci Polym Lett Ed 1985, 23, 103–108.

14 Ober, C. K.; Lok, K. P. Macromolecules 1987, 20, 268–273.

15 Paine, A. J.; Luymes, W.; McNulty, J. Macromolecules 1990, 23, 3104–3109.

16 Paine, A. J. Macromolecules 1990, 23, 3109–3117.

17 Paine, A. J. J Polym Sci Part A: Polym Chem 1990, 28, 2485–2500.

18 Paine, A. J.; McNulty, J. J Polym Sci Part A: Polym Chem 1990, 28, 2569–2574.

19 Paine, A. J. J. Colloid Interface Sci 1990, 138, 157–169.

20 Paine, A. J.; Deslandes, Y.; Gerroir, P.; Henrissat, B. J Colloid Interface Sci 1990, 138, 170–181.

21 Winnik, F. M.; Paine, A. J. Langmuir 1989, 5, 903–910.

22 Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci Part A: Polym Chem 1986, 24, 2995–3007.

23 Wang, D.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. J Appl Polym Sci 2002, 84, 2692–2709.

24 Barrett, K. E. J.; Thomas, H. R. In Dispersion Polymerization in Organic Media; Barrett, K. E. J. Ed.; Wiley: Toronto, 1975; Chapter 4, pp 115–200.

25 Corner, T. Colloids Surf 1981, 3, 119–129.

26 Cawse J. L. In Emulsion Polymerization and Emulsion Polymers; Lovell, P. A.; El–Aasser, M. S., Eds.; Wiley: Toronto, 1997; Chapter 22, pp 744–761.

27 Sulzbacher, M.; Bergmann, E. J Org Chem 1948, 13, 303–308.

28 Overberger, C. G.; Frazier, C.; Mandelman, J.; Smith, H. F. J Am Chem Soc 1953, 75, 3326–3330.

29 Tao, Z.; Yang, W.; Zhou, H.; Wang, C.; Fu, S. Colloid Polym Sci 2000, 278, 509–516.

30 Huang, J.-X.; Yuan, X.-Y.; Yu, X.-L.; Zhang, H.-T. Polym Int 2003, 52, 819–826.

31 Shan, G.-R.; Weng, Z.-X.; Huang, Z.-M.; Pan, Z.-R. J Appl Polym Sci 1997, 63, 1535–1542.

32 Iwatsuki, S.; Kubo, M.; Wakita, M.; Matsui, Y.; Kanoh, H. Macromolecules 1991, 24, 5009–5014.

33 Yamada, Y; Takase, I.; Mishima, T. Kobunshi Kagaku 1967, 24, 326.

34 Kohli, P.; Scranton, A. B.; Blanchard, G. J. Macromolecules 1998, 31, 5681–5689.

35 Schmidt-Naake, G.; Drache, M.; Leonhardt, K. Macromol Chem Phys 1998, 199, 353–361.

36 Beaune, O.; Bessiere, J.-M.; Boutevin, B. Eur Polym J 1992, 28, 1501–1506.

37 Kharas, G. B.; Ajbani, H. J Polym Sci Part A: Polym Chem 1993, 31, 2295–2303.

38 Fox, T. G. Bull Am Phys Soc 1956, 1, 123.

39 Chapin, E. C.; Abramo, J. G.; Lyons, V. L. J Org Chem 1962, 27, 2595–2597.

40 Brostow, W.; Chiu, R.; Kalogeras, I. M.,Vassilikou-Dova, A. Mater Lett 2008, 62, 3152–3155.

41 Grulke, E. A. In Polymer Handbook, 4th ed.; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley-Interscience: Toronto, 1999; pp VII/675.

42 van Krevelen, D. W. Properties of Polymers: Their Correlation with Chemical Structure, 3rd ed.; Elsevier: New York, 1990; Chapter 7.

43 Nair, R.; Nyamweya, N.; Gönen, S.; Martínez-Miranda, L. J.; Hoag S. W. Int J Pharmaceutics 2001, 225, 83–96.