

Effects of Styrene Oligomers and Polymers on the Suspension Polymerization Behavior and Properties of Expandable Polystyrene

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ABSTRACT: Styrene oligomers are formed by a free-radical mechanism during the thermal polymerization of styrene in storage. The effects of these compounds on the preparation of expandable polystyrene (EPS) were investigated with respect to suspension polymerization behavior and the properties of the impregnated polystyrene beads produced. Styrene dimers and trimers up to concentrations of 0.2 wt % did not affect the stability of the suspension during the polymerization and impregnation stages. Besides differentiated effects on the particle size distributions of the polymers and on the polymerization rate, no chain-transfer activity of the oligomers was observed, and this confirmed the assignment of chain transfer to the Diels–Alder dimer in the literature. The investigation of the foaming behavior of the pentane-impregnated EPS

beads indicated a significant reduction of the prefoaming density caused by styrene dimers and trimers. This behavior resulted from a decrease in the glass-transition temperatures of these polymers. The effects of high-molecular-weight polystyrene, formed in addition to oligomers during storage by the thermal polymerization of styrene, on the polymerization behavior and polymer properties of EPS were also investigated. The results showed a significant impact on the suspension stability that was dependent on the concentration of the high-molecular-weight polystyrene. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 453–458, 2008

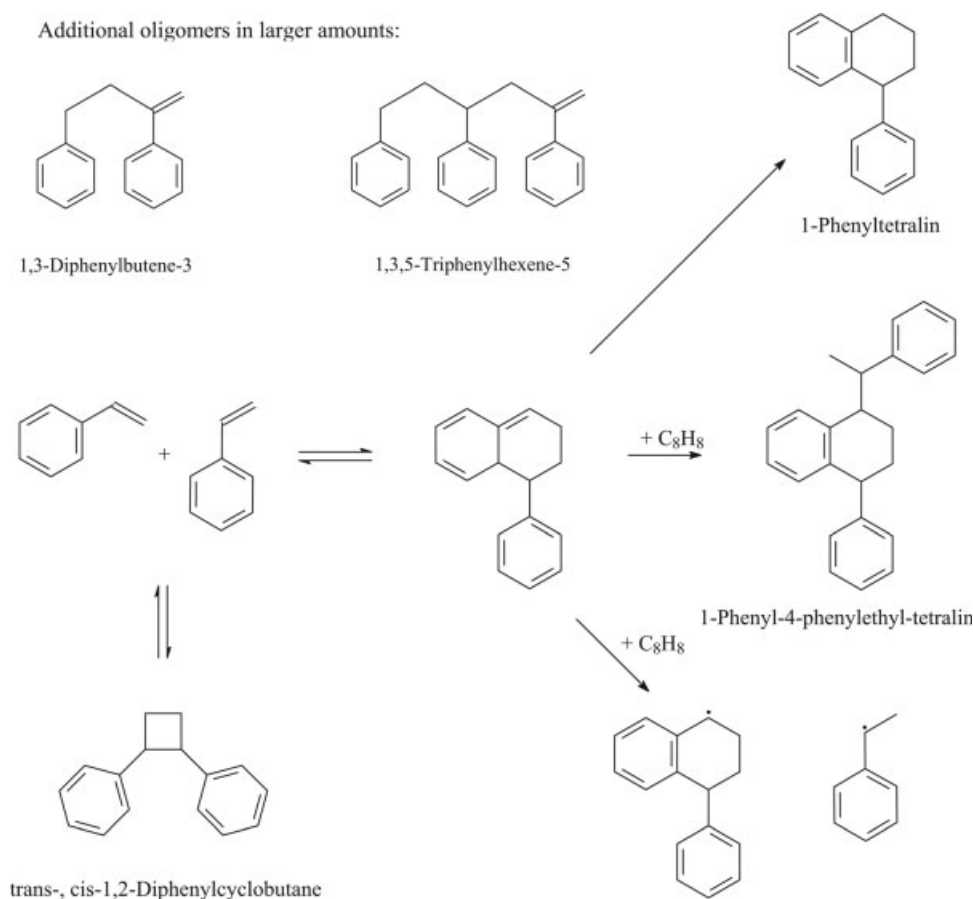
Key words: oligomers; particle size distribution; polystyrene

INTRODUCTION

The appearance and investigation of oligomers of styrene, particularly dimeric and trimeric compounds, during polymerization reactions have attracted the attention of polymer research from the beginning up to the present. Intermediates of the formation of these oligomers have been identified as the active initiating species of the thermal polymerization of styrene (e.g., occurring during monomer storage at the ambient temperature or at desired polymerization temperatures). The generally accepted mechanism of this thermally initiated free-radical polymerization comprising the formation of the main dimers and trimers can be described as shown in Scheme 1.^{1–5} Recently, the formation of oligomers has been of special interest in radiation-induced styrene polymerization and gas-phase thermal polymerization of styrene and in theoretical calculations of the mechanism of the self-initiated thermal polymerization of styrene.^{6–8}

Styrene is used as a monomer for manufacturing expandable polystyrene (EPS) by a suspension polymerization process.^{9,10} Because of the suspension-stabilizing mechanism employed by this process, very small concentrations of chemical compounds, such as styrene dimers and trimers, might have an important impact on polymerization behavior. Of particular concern are the suspension stability and the subsequent particle size distribution of the polystyrene beads formed. Additionally, the properties of the EPS beads and their foaming behavior might be significantly affected by these compounds. Although there has been some investigation of the occurrence of styrene oligomers in polystyrene foams used as food containers,¹¹ no reports have been found in the literature on the effects of styrene oligomers on the suspension polymerization behavior and properties of EPS. Therefore, an investigation of these topics was conducted with styrene dimers and styrene trimers separately. Besides the formation of oligomers, high-molecular-weight polystyrenes might also arise during the storage of the monomer at the ambient temperature. The effects of such impurities associated with the formation of oligomers were also covered by this investigation.

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Scheme 1 Mechanism of the thermally initiated free-radical polymerization of styrene describing the formation of dimers and trimers.

EXPERIMENTAL

Materials

Samples of styrene dimers (labeled DP) and trimers (labeled TP) were obtained by fractional distillation of the condensed heavy components of a devolatilizer recycled from polystyrene fabrication. The samples were obtained as a light yellow, oily liquid (DP) or as an uncolored, viscous oil (TP) at room temperature.

The compositions of the styrene dimer and trimer samples and the structures of the different species were determined after the separation of the fractions of the three dimer peaks and the two trimer peaks. An analysis was performed with size exclusion chromatography (SEC) in tetrahydrofuran (THF) and with subsequent mass spectrometry as well as proton nuclear magnetic resonance analysis in comparison with simulated spectra. The quantitative compositions of the styrene dimer and trimer samples are summarized in Table I. Although *trans*-1,2-diphenylcyclobutane and *cis*-1,2-diphenylcyclobutane were the main components in the styrene dimer, different isomers of 1-phenyl-4-phenylethyl-tetralin were the main components in the styrene trimer.

Samples of high-molecular-weight polystyrenes were obtained from Polymer Laboratories, Ltd. (Shropshire, United Kingdom).

Polymerization procedure

A stirred polymerization reactor was charged with 721 g of H₂O, 3.1 g of tricalcium phosphate (TCP),

TABLE I
Quantitative Compositions of the Styrene Dimer and Trimer Samples

Compound	Structure	Concentration (area % of RI peaks in SEC)
Dimer DP	1,3-Diphenyl-butene-3	12
	<i>trans</i> -1,2-Diphenylcyclobutane and <i>cis</i> -1,2-diphenylcyclobutane	59
	1-Phenyltetralin	16
	Higher oligomers	13
	Trimer TP	1,3,5-Triphenylhexene-5
Trimer TP	1-Phenyl-4-phenylethyl-tetralin (different isomers)	73
	Higher oligomers	8

0.0775 g of calcium carbonate, and 0.0078 g of a costabilizer. Added to the reactor contents at room temperature was a solution of 2.48 g of dibenzoyl peroxide, 1.162 g of *tert*-amylperoxy-2-ethylhexyl carbonate, 1.63 g of dicumyl peroxide, 0.217 g of divinyl benzene (DVB), 0.852 g of polyethylene wax, 5.81 g of hexabromocyclododecane, and the required amount of the oligomer in 775 g of styrene. The polymerization was started by an increase in the temperature to 90°C, and it was continued at this temperature for 4.5 h. After this time, the reactor was closed, and 55.0 g of pentane was added. The polystyrene beads were allowed to be impregnated with pentane for 3 h at 115°C. After cooling to room temperature, the impregnated polystyrene beads were separated from the liquid phase by filtration, centrifugation, and drying under air.

Polymerization conversions were determined by refractive-index (RI) measurements of the organic phase of the polymerizing suspension according to a calibration curve.

Analytical methods

The prefoaming density was determined as the bulk density of the EPS foam beads after the prefoaming of 18.2 g of EPS beads by the addition of steam at atmospheric pressure for 3 min in a glass cylinder by volumetric measurements.

The EPS molecular weight distributions were measured by SEC on an Agilent series 1100 instrument (Agilent Technologies, Inc., Santa Clara, CA) equipped with three 7.5 mm i.d. × 300 mm columns (PLgel 10 μm Mixed-B, Polymer Laboratories). The analyses were carried out in THF at 40°C at an eluent flow rate of 1.0 mL/min. The molecular weights were calculated on the basis of a conventional calibration with EasyCal narrow-distribution polystyrene standards (Polymer Laboratories) and Cirrus gel permeation chromatography/SEC software (Polymer Laboratories).

The differential scanning calorimetry (DSC) traces were recorded with a DSC 7 (PerkinElmer, Waltham, MA). The thinly sliced samples of the foamed EPS beads were heated at a rate of 10 K/min to 200°C to remove the blowing agent pentane. The samples were cooled at a rate of 200 K/min to -30°C. The glass-transition temperatures of the polystyrenes without pentane were determined from a similar second scan.

RESULTS AND DISCUSSION

Effects of dimers and trimers

The influence of styrene dimers and trimers on the suspension polymerization and properties of EPS

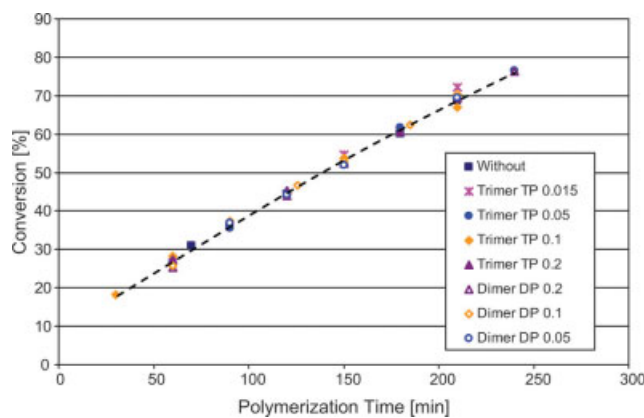


Figure 1 Dependence of the polymerization conversion on the polymerization time at different styrene dimer and trimer concentrations (wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was investigated. Oligomers, up to a concentration of 0.2 wt %, were added to the styrene monomer before polymerization.

Neither styrene dimers nor trimers in the investigated range had any negative effect on suspension stability during the polymerization phase or during the impregnation stage with the blowing agent pentane, in contrast to what has been observed with some agents, such as alkyl benzene sulfonates,¹⁰ that actively affect the stability of the styrene-water interface. This indicates that the styrene dimers and trimers remained enclosed within the styrene/polymer beads and did not accumulate at the interface to the aqueous phase.

Figure 1 indicates there was no important effect of the styrene dimers and trimers on the suspension polymerization behavior of styrene up to conversions of about 75% at the oligomer concentrations investigated. However, at the end of the polymerization and impregnation stages, styrene residue, as determined by headspace gas chromatography (Table II), increased, especially at higher oligomer concentrations. This suggested a slight reduction of the polymerization rate. This behavior might be a result of the dilution of the styrene monomer by the oligomers, as also observed in the polymerization of styrene with the addition of a low-molecular-weight solvent, such as ethyl benzene, or in the presence of a higher level of ethyl benzene as a monomer impurity in styrene.

In agreement with the aforementioned suspension stability findings, styrene trimers did not show an important effect on the particle size distribution of the impregnated polystyrene beads produced (Table II), as determined by sieve analysis, with the *C* value as the median particle diameter and the coefficient of variation as an indication of the broadness of the particle size distribution. However, lower amounts

TABLE II
Effect of Styrene Oligomers on the Polymer Properties

Oligomer	Oligomer concentration (wt %)	C value (mm)	Coefficient of variation (%)	Styrene residue (ppm)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
None		0.96	42.3	771	77,000	229,300	2.98
Trimer TP	0.0015	0.74	46.6	899	77,200	230,700	2.99
Trimer TP ^a	0.05	0.97	44.0	—	—	—	—
Trimer TP	0.10	0.92	42.5	1086	79,000	238,900	3.03
Trimer TP	0.20	0.96	41.7	1355	79,000	236,200	2.99
Dimer DP	0.05	1.02	45.2	808	78,300	234,100	2.99
Dimer DP	0.10	1.24	37.6	730	79,100	239,000	3.02
Dimer DP	0.20	0.64	48.1	1088	78,100	232,600	2.98

^a Without DVB.

of dimers seemed to increase the EPS particle size, whereas higher amounts led to decreased particle size. Some selected particle size distributions according to the technically relevant particle size ranges of EPS are shown in Figure 2.

The results of the measurements of the number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (M_w/M_n) of the polystyrenes prepared in the presence of styrene oligomers (Table II) did not show any considerable changes and therefore did not indicate any chain transfer or other activity for the dimers or trimers. These results confirm the literature assignment of chain-transfer activity to the Diels–Alder dimer occurring in oligomers immediately formed in the thermal polymerization of styrene;¹² this is, however, absent in the case of the oligomers added to the EPS polymerization, and so chain transfer does not appear.

The first observation of the foaming behavior of the pentane-impregnated EPS beads in a boiling water bath showed that the foamed EPS particles possessed a smooth surface and a fine-cell foam in the presence of dimers and trimers. In a further

detailed analysis of the foaming properties of the EPS beads, surprisingly, it was observed that the prefoaming density of the foamed EPS particles (as a measure of the lowest foam density achievable after a predetermined time of steam treatment) decreased with an increase in the dimer or trimer concentration, as shown in Figure 3. In general, the prefoaming density of the foamed EPS particles decreased by roughly 1 g/L with an increase in the oligomer concentration of 0.2 wt %. The styrene dimer seemed to cause a slightly higher decrease of the prefoaming density in comparison with the trimer.

To investigate the reason for this behavior, a thermal analysis of the EPS beads liberated from pentane as the blowing agent was performed by DSC. As a result, a change in the glass-transition temperature of the polystyrenes was observed, and it was dependent on the type of oligomer and on the oligomer concentration (Fig. 4). The reduction of the glass-transition temperature with an increasing oligomer concentration was also confirmed by the onset glass-transition temperatures of the polymers. Increasing the oligomer concentration by 0.2 wt %

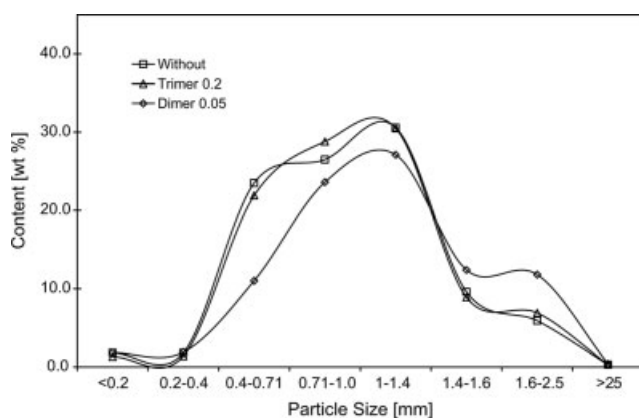


Figure 2 Selected particle size distributions of EPS with styrene dimers and trimers (concentrations are given as weight percentages).

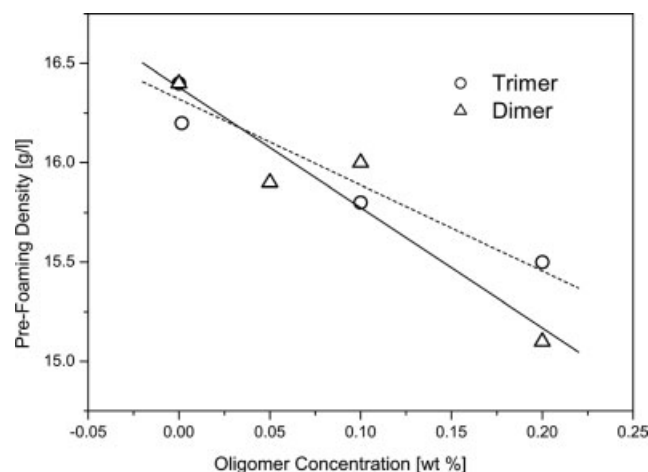


Figure 3 Dependence of the prefoaming density of EPS on the oligomer concentration.

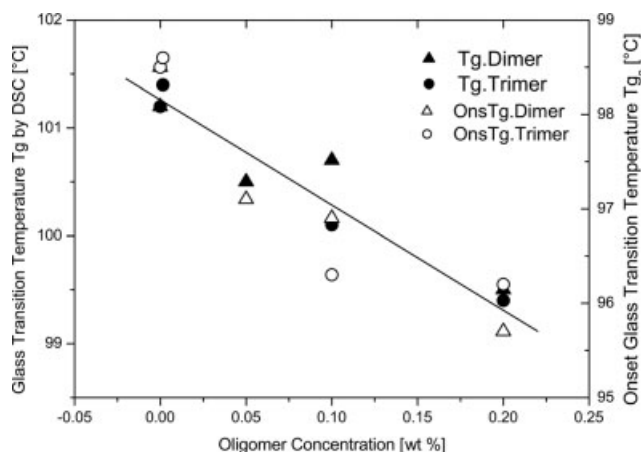


Figure 4 Dependence of the glass-transition temperature and onset glass-transition temperature of polystyrene on the oligomer concentration.

reduced the glass-transition temperature by about 1.9°C.

Thus, the lower glass-transition temperature of the polystyrene beads containing styrene oligomers seemed to be primarily responsible for the decrease in the prefoaming density of the EPS beads with an enhanced oligomer concentration. The lower glass-transition temperature allowed earlier softening of the polymer phase during the steam treatment and therefore longer exposure to the expansion by the blowing agent pentane, resulting in a more voluminous polymer foam, as indicated by a lower prefoaming density of the EPS.

Effect of high-molecular-weight polystyrenes

The appearance of styrene dimers and trimers during storage of styrene monomer is an indication of an accompanying thermal polymerization of styrene. Despite the low amounts of polymers formed, the degree of polymerization is very high because of the relatively low polymerization temperature. These high-molecular-weight polymers might affect a later suspension polymerization significantly. Thus, the effects of such impurities on EPS suspension polymerization were investigated with different concentrations of high-molecular-weight, molecularly uniform polystyrenes of a peak molecular weight (M_p) of about 10,000,000 g/mol ($M_w/M_n = 1.09$).

At relatively high concentrations (0.1 and 0.2 wt %) of high-molecular-weight polystyrenes (Fig. 5), there did not appear to be a significant effect of the added polymers on the suspension polymerization behavior of styrene until conversions of about 50%. However, at higher conversions above about 55%, the polymerizing suspension was unstable in the presence of high-molecular-weight polystyrenes of these concentrations. This is a surprising effect, especially in

view of the addition of much larger quantities of polystyrenes, with a much lower M_w value of about 200,000 g/mol, in industrial EPS processes to reuse undesirable EPS side fractions without affecting the suspension stability.⁹

A stable suspension during polymerization was achieved by a significant reduction of the amount of the high-molecular-weight polystyrenes to concentrations of 0.02 wt % and lower as well as an enhancement of the amount of the suspension stabilizer TCP (Table III). In general, the particle size of the impregnated polystyrene beads, as indicated by the C value, increased with an enhanced amount of the high-molecular-weight polystyrene added to the suspension (see the C values of the polymers at the same TCP concentration of 0.36 wt %). Regarding the further results shown in Table III, it has to be considered that, at the same concentration of added high-molecular-weight polystyrene, an increased amount of the suspension stabilizer TCP led to better suspension stabilization, resulting in a lower EPS particle size. Much larger amounts of the high-molecular-weight polystyrenes (0.1 and 0.2 wt %), as used previously, subsequently led to a further coarsening of the EPS particle size, resulting in complete instability of the polymer suspension.

Obviously, the instability of the polymer suspension at higher conversions by the addition of higher amounts of extremely high-molecular-weight polystyrenes (0.1 or 0.2 wt %) might be caused by a disturbance in the equilibrium between breakage and coalescence of the dispersed highly viscous styrene/polymer phase. This critical range of particle formation is characterized by an increasing particle size as well as a broadening of the particle size distribution slightly below a conversion of about 60% by the extremely long polystyrene chains added. This disturbance results in an uncontrolled coarsening of the dispersed phase and, finally, in complete instability of the suspension at this conversion.¹⁰

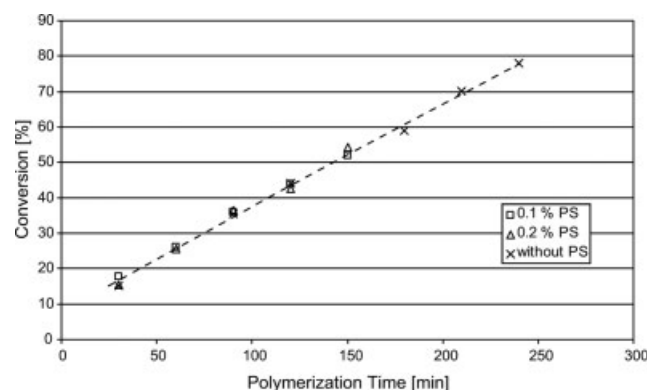


Figure 5 Conversion-time curves of suspension polymerizations with styrene containing high-molecular-weight polystyrene (PS; $M_p = 11,400,000$ g/mol) as an impurity.

TABLE III
Effect of High-Molecular-Weight Polystyrene as an Impurity in the Styrene Monomer on the Polymer Properties ($M_p = 11,400,000$ g/mol)

High-molecular-weight polystyrene concentration (wt %)	TCP concentration (wt %)	C value (mm)	Coefficient of variation (%)	Styrene residue (ppm)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
0	0.34	1.35	38.3	838	78,700	229,300	2.91
0.005	0.36	1.23	37.8	728	79,400	233,000	2.93
0.01 ^a	0.36	1.89	33.0	893	79,600	237,600	2.99
0.02	0.44	1.19	40.8	813	78,400	238,000	3.04

^a $M_p = 9,835,000$ g/mol.

In agreement with the conversion–time curves in Figure 5, the styrene residue of the EPS beads after polymerization and impregnation did not vary importantly (Table III). The slight increase in M_w and M_w/M_n was a result of the addition of polystyrenes of extremely high molecular weights. In contradiction to the findings on the addition of oligomers, the prefoaming density of the foamed EPS beads did not show considerable changes with the addition of the high-molecular-weight polystyrenes in concentrations up to 0.02 wt %.

CONCLUSIONS

Styrene dimers and trimers were prepared as well-characterized fractions of styrene oligomers. Up to concentrations of 0.2 wt %, the dimers and trimers did not affect the stability of the suspension during the polymerization and impregnation stages of EPS. Besides differentiated effects on the particle size distributions of the polymers and on the polymerization rate, no chain-transfer activity of the oligomers was observed, and this confirmed the assignment of chain transfer to the Diels–Alder dimer in the literature. The investigation of the foaming behavior of the pentane-impregnated EPS beads indicated a significant reduction of the prefoaming density by styrene dimers and trimers. In general, the prefoaming density of the foamed EPS particles decreased by roughly 1 g/L with an increase in the oligomer concentration of 0.2 wt %. The styrene dimer seemed to cause a slightly higher reduction of the prefoaming density in comparison with the trimer, probably because of a decrease in the glass-transition temperature. Increasing the oligomer concentration by 0.2 wt % caused the glass-transition temperature to decrease by about 1.9°C.

The effects of high-molecular-weight polystyrenes on the polymerization behavior and polymer proper-

ties of EPS were also investigated, and we found a significant impact on the suspension stability dependent on the concentration. In general, the particle size of the impregnated polystyrene beads increased with an enhanced amount of the high-molecular-weight polystyrene ($M_p \approx 10,000,000$ g/mol) added to the suspension (up to about 0.02 wt %). Much larger amounts of the high-molecular-weight polystyrenes (0.1 and 0.2 wt %) led to a further coarsening of the EPS particle size, resulting in complete instability of the polymer suspension.

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