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Anionic Dispersion Polymerization of 1,4-Divinylbenzene

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ABSTRACT: Highly cross-linked 1,4-divinylbenzene (1,4-DVB) microgels with a shell of poly(4-*tert*-butylstyrene) (PtBS) chains were prepared by anionic dispersion polymerization in *n*-heptane at 50 °C. "Living" PtBS chains with various lengths were used as the initiator of the DVB polymerization and also as steric stabilizers for the phase-separated particles. The effect of the polymerization parameters such as the length of PtBS chains and the DVB concentration on the properties of the microgels was studied using static and dynamic light-scattering techniques and viscosimetry. As the DVB concentration in the reaction medium increases, both the molecular weight of the microgels and their intrinsic viscosities increased, at first slowly and then abruptly at about 30-35 mol % DVB, corresponding to the transition from the microgel to the macrogel region. It was also found that the length of PtBS chains at the nuclei surface controls the intrinsic viscosities of the microgels. The calculations indicate that the solvated PtBS chains are close-packed on the surface of the nuclei. A mechanism for microgel formation and growth in the anionic dispersion polymerization is presented which consists of three stages: (1) DVB polymerization in a homogeneous solution up to the critical micelle concentration of PtBS-poly(4-vinylstyrene) block copolymers formed, (2) fast polymerization and cross-linking reactions within the microgel nuclei, and (3) polymerization at the nuclei surface leading to interparticular reactions.

Introduction

Nonaqueous polymer dispersions are generally prepared by the polymerization of a monomer dissolved in an organic diluent, which is a nonsolvent for the resulting polymer.[1] The polymerization system is thus initially homogeneous, but the polymer chains formed precipitate from the solution after attaining a critical size. In contrast to the precipitation polymerization, a polymeric stabilizer is needed during the reaction to prevent flocculation and agglomeration of the precipitated particles. Generally, amphipathic block or graft copolymers or their precursors are used to stabilize the polymer particles.[1-4] The anchor block of the stabilizer, which is insoluble in the continuous phase, adsorbs on the precipitated polymer particle, and the solvated block extends away from the particle surface and prevents the particles from flocculation by a mechanism known as steric stabilization.

A further method of carrying out the dispersion polymerization process is to prepare the "living" soluble block first, to which the disperse phase monomer is added to continue growth from the living end.[1] After reaching a critical degree of monomer conversion, a phase separation takes place during the reaction and the block copolymers formed precipitate from the solution in the form of aggregates, which are stabilized by the solvated blocks at their surface. Barrett has reported the preparation of polystyrene dispersions in *n*-heptane using living poly(4-*tert*-butylstyrene) (PtBS) chains.[1] The particle diameter was found to vary between 30 and 100 nm depending on the amount of styrene used. PtBS has a solubility parameter (δ) of 8.12 $(\mathrm{cal/cm^3})^{1/2}$ in contrast to the value of 9.1 $(\mathrm{cal/cm^3})^{1/2}$ for polystyrene.[5,6] Thus it can be expected that in *n*-heptane with $\delta = 7.4\ (\mathrm{cal/cm^3})^{1/2}$ the solvated PtBS blocks form a steric layer around the polystyrene nuclei, thus imparting stability.

The dispersion polymerization of 1,4-divinylbenzene (1,4-DVB) in organic media has, to our knowledge, not been reported previously. For the synthesis of 1,4-DVB polymer particles of colloidal size, called reactive microgels,[7] two methods have been applied; one is the polymerization in highly dilute solution, in which intramolecular cross-linking is favored.[8,9] The other method is the polymerization in an emulsion in which the cross-linking reactions are limited to colloidal particles.[10-14] In both cases, however, the isolation and storage of reactive microgels are rather difficult and require careful procedures due to the pendant double bonds at their surfaces, which may react easily with each other to form insoluble agglomerates.

In this study, we present the use of living PtBS chains as an initiator and also as a steric stabilizer in the dispersion polymerization of 1,4-DVB. A similar procedure is known to be applied to the synthesis of star-shaped polymers; namely, living polymer chains are used to initiate the polymerization of the DVB monomer.[15,16] However, by this technique, the polymerization reaction proceeds in a homogeneous solution and only a small amount of DVB is used as the linking agent of the polymer precursors. The aim of this work was primarily to study the formation of microgel particles in nonaqueous dispersions, but these studies are also of inherent interest to prepare stable microgel particles with a protective layer at their surfaces. The experiments were carried out at 50 °C in *n*-heptane. The molecular weight of living PtBS chains and the DVB concentration were varied over a wide range. The overall copolymer concentration in the final dispersions ranged between 4 and 6%.

Experimental Section

Materials. 4-*tert*-Butylstyrene (tBS) was prepared from 4-*tert*-butylbenzene as described in refs 17 and 18. Purity was checked by GC and found to be 98%, the rest being 3-*tert*-butylstyrene. 1,4-DVB was separated from the commercial mixture (BAYER AG) using the copper chloride method.[19] 1,4-DVB was then further purified by crystallization from methanol. Its purity was 96%. 1,4-DVB was distilled twice over a slurry of ground calcium hydride, diluted to a 50% solution in *n*-heptane and stored at approximately -18 °C until use. *sec*-Butyllithium (*sec*-BuLi, Aldrich) as a 12% solution in cyclohexane/isopentane mixture was used without further treatment. Its concentration was determined by the Gilman-

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Table I
d*n*/d*c* Values of PtBS and Pure 1,4-DVB Microgels at 25 °C and at 633 nm

polymer	solvent toluene	 cyclohexane
PtBS	0.059	0.129
1,4-DVB microgel	0.13	0.17[a]

[a] d*n*/d*c* value of polystyrene in ref 6.

Haubein double titration method.[20] *n*-Heptane (Merck pa) was refluxed over sodium for at least 24 h and distilled twice under nitrogen atmosphere. It was then degassed under vacuum by repeated freeze–thaw cycles. After addition of a given amount of *sec*-BuLi via syringe to yield a final *sec*-BuLi concentration of 1%, *n*-heptane was freshly distilled under purified nitrogen.

Polymerization. All experiments were carried out under purified nitrogen. A 200-mL cylindrical reactor equipped with a Teflon-covered magnetic stirring bar and two rubber septums was dried at approximately 600 °C under vacuum and filled with nitrogen. To this was added 50 mL of *n*-heptane by means of a syringe. It was then degassed by three freeze–thaw cycles, and nitrogen gas was introduced. Then the reactor was set in a thermostated bath at 50 °C; after equilibrium, a given amount of *sec*-BuLi solution and then 2.5 mL of tBS were added via syringes. The reaction was complete after 3 h. A small amount of the heptane solution was then removed from the reactor and terminated with methanol. The polymer was isolated and used for molecular weight determination of soluble macromolecules thus obtained. Under the experimental conditions, the molecular weight distribution of soluble chains ($\bar{M}_w/\bar{M}_n$) was found to be about 1.1.

To the heptane solution of living PtBS chains at 50 °C, 1,4-DVB solution in heptane was added dropwise by means of a syringe within 10 min under vigorous stirring. During the addition of the DVB monomer, the color turns from yellow-orange to dark red. The polymerization was then continued for 2 h at 50 °C. The reaction mixture was then cooled down to 0 °C and terminated with methanol. All dispersions were precipitated in methanol, and the polymer was isolated by freeze-drying from benzene for at least 24 h. Homologous series of 1,4-DVB microgels were prepared in this way, allowing systematic variation of the molecular weight of PtBS chains and the DVB concentration. The final microgel concentration in the reaction batch ranged between 4 and 6%.

Characterization. All solvents were purified and distilled prior to use. Solvent purity was checked by GC and found to be nearly 100%. The weight-average molecular weight of the microgels ($\bar{M}_w$) was determined by small-angle light scattering (Chromatix KMX-6) at 25 °C with a laser source at 633 nm. Toluene and cyclohexane were used as the solvents of the microgels.

The refractive index increments (d*n*/d*c*) were measured with a Chromatix KMX-16 refractometer. The measured d*n*/d*c* values of the microgels were found to be in good agreement with the calculated values according to the additivity rule.[21] As seen in Table I, the d*n*/d*c* values of PtBS and pure 1,4-DVB microgels in toluene are very different, and, thus, instead of the true weight-average molecular weight of the microgels, only an apparent value can be obtained using light-scattering measurements.[21] However, the measurements carried out with samples with $M_w < 700\,000$ g/mol in two different solvents (toluene and cyclohexane) gave very similar values, so that the difference between the apparent and true values can be expected to be small.

Quasielastic light-scattering experiments were performed using PCS 100 spectrometer and K 7027 "Loglin" correlator (Malvern Ins. Ltd.) with a Spectra-Physics argon-ion laser (Model 2020-03) at 488 nm. The measurements were carried out at 20 °C in *n*-heptane and at a polymer concentration of about 0.2%. The scattering angle was 90°. The data were analyzed and the *z*-average hydrodynamic diameter (D_z) and the particle size distribution of the samples were calculated using the methods of cumulants[22] and exponential sampling[23] (Autosizer II), respectively.

The number-average molecular weight of PtBS ($\bar{M}_{n,s}$) was measured in toluene at 61 °C using a Knauer vapor pressure osmometer. Dilute solution viscosities of the microgels were measured in toluene at 20 °C by AVS 400 Schott. Intrinsic viscosities ($[\eta]$) were obtained by extrapolating plots of η_{sp}/c vs c to zero concentration where η_{sp} is the specific viscosity of a solution of concentration c (in grams per milliliter). The content of double bonds in the microgels was measured by IR spectroscopy[24] (Philips SP3-200).

Results and Discussion

Microgel Synthesis. The conditions of synthesis and the properties of the resulting microgels are given in Table II. The molecular weight of living PtBS chains used was varied between 3000 and 20 000 g/mol. The DVB concentrations are expressed as the mol ratio of 1,4-DVB to PtBS (R) and also as the mole fraction of 1,4-DVB units in the microgels (n_{DVB}). Table II also contains the molecular weight of the microgel nuclei ($\bar{M}_{w,nuclei}$) and the average number of PtBS chains surrounding one microgel nucleus, which corresponds to the aggregation number of the nuclei (Q). These quantities were calculated using the equations

$$\bar{M}_{w,nuclei} = \bar{M}_w m_{DVB} \tag{1}$$

$$Q = (\bar{M}_w/\bar{M}_{n,s})(1 - m_{DVB}) \tag{2}$$

where $\bar{M}_w$ and $\bar{M}_{n,s}$ are the molecular weight of the microgel and the soluble chains (PtBS), respectively, and m_{DVB} is the weight fraction of 1,4-DVB units in the microgels.

The results show that both the molecular weight of the microgels ($\bar{M}_w$) and the aggregation number of the nuclei (Q) increase with increasing DVB concentration in the reaction medium. In Figure 1, the values $\bar{M}_w$ and Q are plotted against the DVB concentration expressed in terms of R (the mol ratio of 1,4-DVB to PtBS). As the DVB concentration increases at a fixed length of soluble chains, the change in the values of $\bar{M}_w$ and Q is at first slow and then abruptly increases in a critical range of the DVB concentration (R_{cr}). A further increase in the amount of DVB above R_{cr} results in the formation of stable milky dispersions of copolymer particles, which are insoluble in benzene. Thus, R_{cr} represents the critical DVB concentration in the reaction medium for transition from the microgel to the macrogel region. A further point shown in Figure 1 is that the value R_{cr} increases with the increasing length of living soluble chains. However, as seen in Table II, the DVB content of the microgels at these transition regions remains constant and is independent of the length of PtBS chains. All the experimental data shown in Figure 1 are collected in Figure 2 as the dependence of the molecular weight of the microgel nuclei ($\bar{M}_{w,nuclei}$) on the DVB content of the microgels (n_{DVB}). The plot of $\bar{M}_{w,nuclei}$ vs n_{DVB} fits to a single curve within the limits of experimental error, regardless of the molecular weight of PtBS. The transition from the microgel to the macrogel region takes place at n_{DVB} = 0.30–0.35 mol/mol. Thus, it can be concluded that longer, solvated chains are capable of solubilizing more DVB molecules than the shorter chains, but the length ratio of insoluble to solvated blocks at the transition regions is constant at a given polymer concentration and temperature.

All of the samples given in Table II are completely soluble in toluene, and no macrogel particles were observed after the reaction. Previously, Hiller showed that the anionic polymerization of 1,4-DVB under the same monomer and initiator concentrations, but with *n*-BuLi in benzene at 20 °C or in hexane/THF mixtures at −78 °C, leads to the formation of insoluble macrogel particles within

Table II
Synthesis Conditions and Properties of Microgels[a]

sample	$\bar{M}_{n,s}$, g/mol	R	n_{DVB}	c, w/v %	$10^{-3}\bar{M}_w$, g/mol	$10^{-3}\bar{M}_{w,nuclei}$, g/mol	Q	$[\eta]$, mL/g	D_z, nm	PV, %
1A	3400	3.6	0.144	4.9	60	7.2	15.5	6.6	12	38
2A	3200	6.7	0.252	5.5	280	60.2	69	7.6	20	42
3A	2700	7.1	0.296	5.6	17000	4300	4700	11.7	99	
4A	3000	9.4	0.333	6.0	12000	3500	2800	13.0	84	43
1B	5200	6.3	0.163	4.8	120	16.4	20	7.7		
2B	5200	9.0	0.217	5.1	275	50.6	43	7.9	27	35
3B	4900	10.7	0.258	5.5	625	137.5	100	8.9	27	38
4B	4300	11.5	0.300	4.7	650	168	112	8.5	31	
5B	4600	13.3	0.317	5.9	1000	274	158	9.0	40	
6B	4000	13.3	0.346	6.1	3000	900	524	11.4	54	
7B	4600	15.8	0.355	6.2	6000	1850	900	13.3	65	37
1C	13000	14.2	0.148	5.0	190	23.6	12.8	10.3	30	40
2C	14000	34.4	0.282	5.7	1300	314.6	70	11.5	41	42
3C[b]	16500	36.3	0.261	4.7	18000	4000	850	15.6	113	34
4C[b]	14000	40.7	0.317	5.2	27000	7400	1400	18.6	140	34
1D[b]	20000	11.4	0.083	4.2	230	15.9	10.7	15.3	30	33
2D[b]	18000	26.4	0.190	4.4	1000	160	47	14.4	34	28

PtBS ($\bar{M}_n$ = 3200–3400 g/mol): $[\eta]$ = 3.6–3.8 mL/g
($\bar{M}_n$ = 4300–4600 g/mol): $[\eta]$ = 4.5–4.7 mL/g
($\bar{M}_n$ = 13000 g/mol): $[\eta]$ = 6.9 mL/g

[a] $\bar{M}_{n,s}$, $\bar{M}_w$, and $\bar{M}_{w,nuclei}$ are the molecular weight of PtBS, microgel, and microgel nuclei, respectively, R is the mole ratio of 1,4-DVB to PtBS, n_{DVB} is the mole fraction of DVB units in the microgels, c is the microgel concentration in the final dispersion, Q is the number of PtBS chains per nuclei, and PV is the percentage of the DVB units in the nuclei with pendant double bonds. [b] The soluble chains in these experiments were prepared using n-BuLi as the initiator, in amounts more than calculated from stoichiometry.

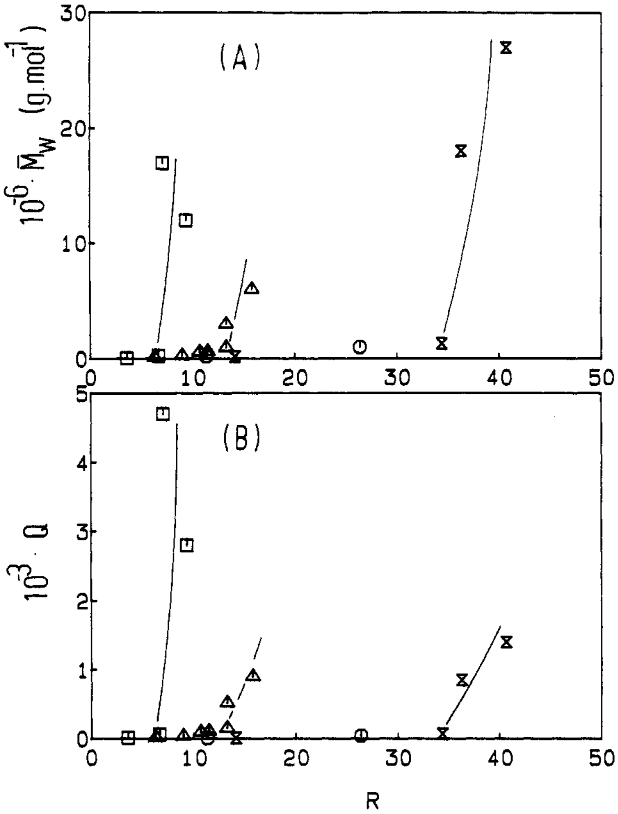

Figure 1. Molecular weight of the microgels $\bar{M}_w$ (A) and the aggregation number of the nuclei Q (B) shown as a function of the mole ratio of 1,4-DVB to PtBS (R): $10^{-3}\bar{M}_{n,s}$ = 2.7–3.4 (□); 4–5.2 (△); 13–16.5 (⧗); 18–20 g/mol (○).

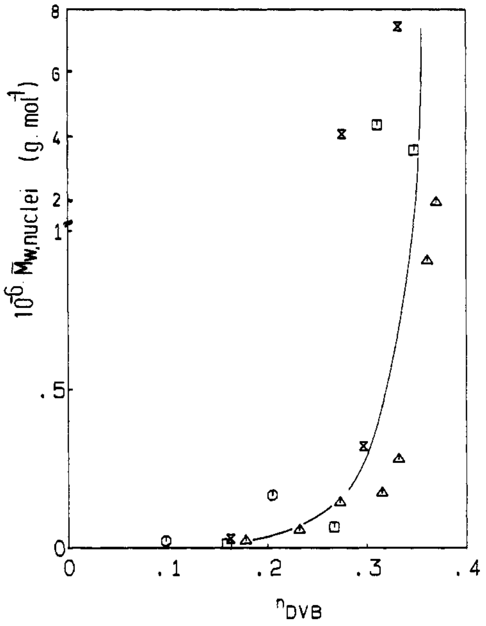

Figure 2. Dependence of the molecular weight of the microgel nuclei $\bar{M}_{w,nuclei}$ on the mole fraction of 1,4-DVB units in the microgels, n_{DVB} (see Figure 1 caption).

2–30 min.[25] Thus, our results demonstrate that the PtBS chains are effective stabilizers for 1,4-DVB microgel particles dispersed in n-heptane.

In all samples, 60–70% of the DVB units were found to be incorporated into the nuclei via both vinyl groups (Table II). This value is very high, in contrast to the values reported in the literature for anionically prepared 1,4-DVB polymers,[25,26] and indicates the highly cross-linked structure of our samples.

Figure 3 shows the hydrodynamic diameters (D_z) and the intrinsic viscosities ($[\eta]$) of the samples plotted against the DVB concentration in terms of its mole fraction (n_{DVB}). As with the previous results, the change in the values of D_z and $[\eta]$ is at first slow and then abruptly increases with the increasing content of the DVB monomer. The critical DVB concentration at the microgel–macrogel transition was also found to be 0.30–0.35 mol/mol (DVB + tBS).

Figure 3 and Table II also contain the intrinsic viscosities of free PtBS chains measured under the same conditions as the microgels. It can be seen that, although the molecular weight of the microgels is 20–6000 times higher than that of the individual soluble chains, the differences between their intrinsic viscosities are very small; the microgels exhibit intrinsic viscosities that are only 1.5–3 times larger than those of the soluble chains. These results are a further proof for the highly cross-linked compact structure of the microgel samples. It is also inter-

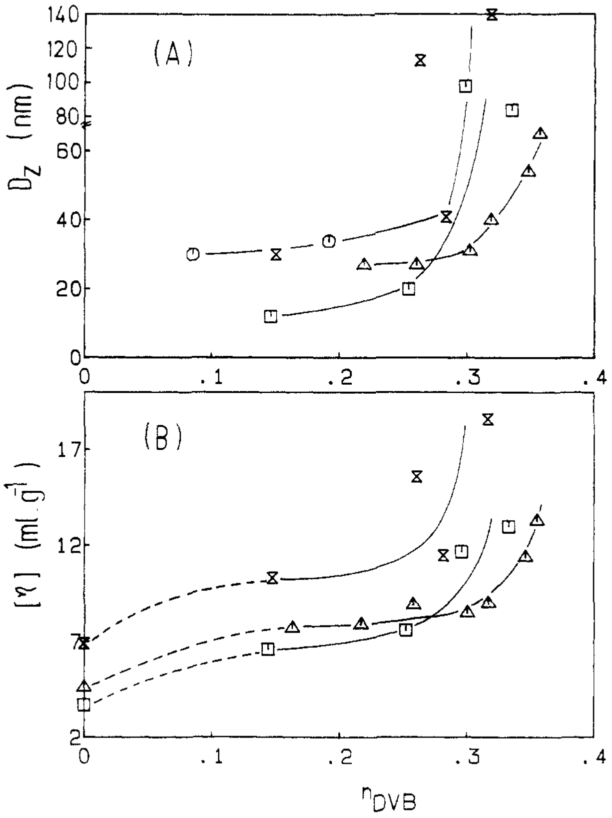

Figure 3. Hydrodynamic diameter (D_z) and intrinsic viscosity ($[\eta]$) of the microgels shown as a function of the mole fraction of 1,4-DVB units in the microgels, n_{DVB} (see Figure 1 caption).

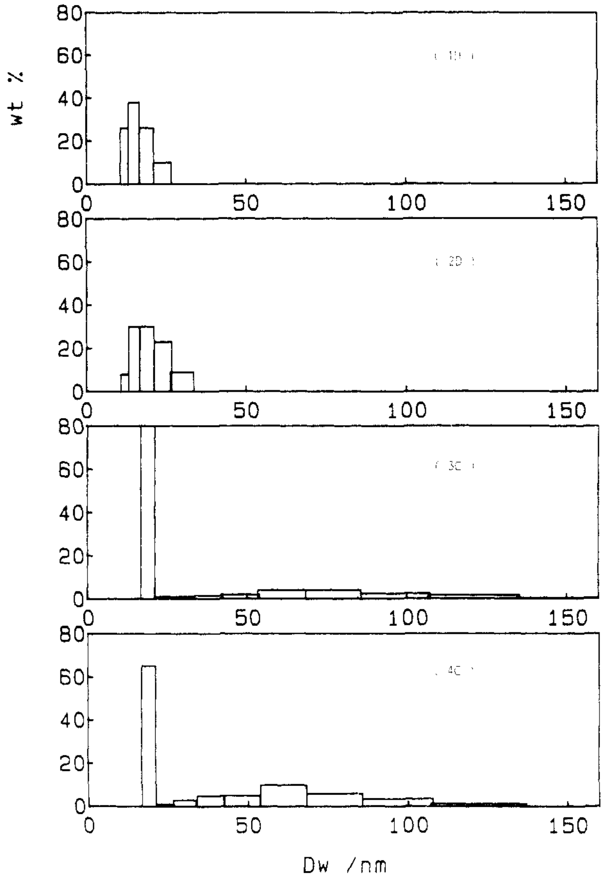

Figure 4. Particle size distribution (by weight) of the microgels in n-heptane. The numbers correspond to the sample numbers in Table II.

esting to compare the intrinsic viscosities of the microgels prepared below the transition region and at different lengths of PtBS (Figure 3); the higher the intrinsic viscosity of the soluble chains, the higher the intrinsic viscosity of the resulting microgels. Thus, the intrinsic viscosity of the soluble chains, i.e., their hydrodynamic volume, controls the hydrodynamic volume of the resulting microgels.

Particle size distributions of the samples were measured in n-heptane using quasielastic light scattering. Figure 4 shows the size distribution of the microgels prepared at $M_{n,s}$ = 14 000 – 20 000 g/mol and at different DVB concentrations. It is surprising that, in all samples, particles of about 15–30 nm in diameter are dominant. The size of these particles does not change with increasing DVB concentration, but their amount decreases from 100 to 65%; there is a corresponding increase in the particles with diameters to 50–100 nm. Similar results were also observed with the other samples. A comparison of these results with M_w and $[\eta]$ values of the microgels indicates that the appearance of these larger particles is responsible for an abrupt increase in the values of M_w and $[\eta]$ at the transition from the microgel to the macrogel region.

Reaction Mechanism. The experimental results can be explained by the following mechanism of microgel formation and growth in the anionic dispersion polymerization (Figure 5):

At the onset of the reaction, a homogeneous solution of living PtBS chains is present in the system (A). Each of the soluble chains has one living end; thus, upon addition of 1,4-DVB monomer, the linear insoluble polymer chains are beginning to grow from the living ends. As in the anionic polymerization the reactivity of the double bonds in 1,4-DVB is 10-fold greater than the pendant double bonds,[27] and essentially linear poly(4-vinylstyrene) (PVS) chains must be formed at this stage of the reaction (B).

Due to the repulsive interactions between the incompatible blocks in PtBS–PVS block copolymers, they may form micelles in selective solvents such as in n-heptane used in this study. Up to a certain concentration, such copolymers are known to be existing as free chains in solution and above this concentration, corresponding to the critical micelle concentration (cmc); almost all additional chains enter in the micellar phase. Both the theoretical and experimental results indicate that the cmc decreases as the relative length of the insoluble block increases or as the solubility of the soluble block decreases.[28,29] As we are working at an almost constant polymer concentration, the cmc can be reached with increasing the length of the PVS block, i.e., with increasing the conversion of the 1,4-DVB monomer.

When the linear insoluble PVS portion of the chains reaches the size at which the cmc is exceeded, aggregates of block copolymers are formed (C). PVS blocks form the nuclei due to their unfavorable interactions with the solvent and absorb monomer from the continuous phase, while the solvated PtBS blocks extend into the solution and form steric layers around the nuclei. For the DVB concentrations below cmc, some cross-linking reactions in the continuous phase are needed for the formation of copolymer aggregates.

The dispersion polymerization then proceeds within the aggregates as in the bulk polymerization; the solvated monomers absorbed are converted into the polymer, and the cross-linking reactions between and within the chains occur intensively due to the high polymer concentration in the nuclei. This yields highly cross-linked nuclei that are not swellable with monomer (D). Accordingly, only

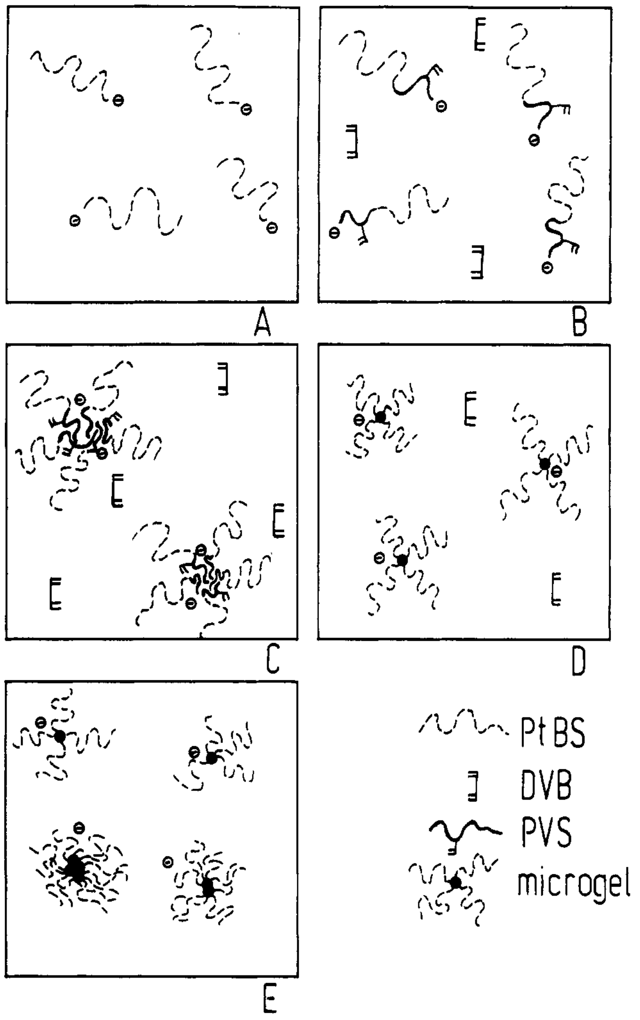

Figure 5. Schematic illustration of the mechanism of microgel formation in the anionic dispersion polymerization.

the amount of monomer initially present in the aggregates is available for the nuclei. Thus, with increasing DVB concentration the growth of the nuclei takes place at a slow rate, as was found experimentally below the transition region.

At this stage, if an excess of monomer is present in the continuous phase, it can only react with the living ends at the surface of the nuclei. These reactions are expected to lead to the formation of bridges between the nuclei and to the appearance of agglomerates with various sizes as illustrated by E in Figure 5 and by Figure 6. The dramatic increase in the values of M_w, $[\eta]$, and D_z and formation of random-sized particles with larger sizes at the transition region from microgel to macrogel can be explained as a result of agglomeration of the primary nuclei. It must be pointed out that an alternative model leading to the agglomerates is the interparticular reactions between the pendant vinyl groups and the living ends at the nuclei surfaces (Figure 6). These reactions can proceed even in the absence of the unreacted DVB monomer. According to this model of agglomeration, the surface area of the nuclei increases with increasing conversion of the DVB monomer, and, therefore, the solvated PtBS blocks around the nuclei become insufficient to stabilize the particles and the particles agglomerate. However, as the calculations in the next section show, the surface of the nuclei is totaly covered by the solvated PtBS chains. Therefore, the agglomeration of the particles using the bridge formation seems to be more plausible than the second model.

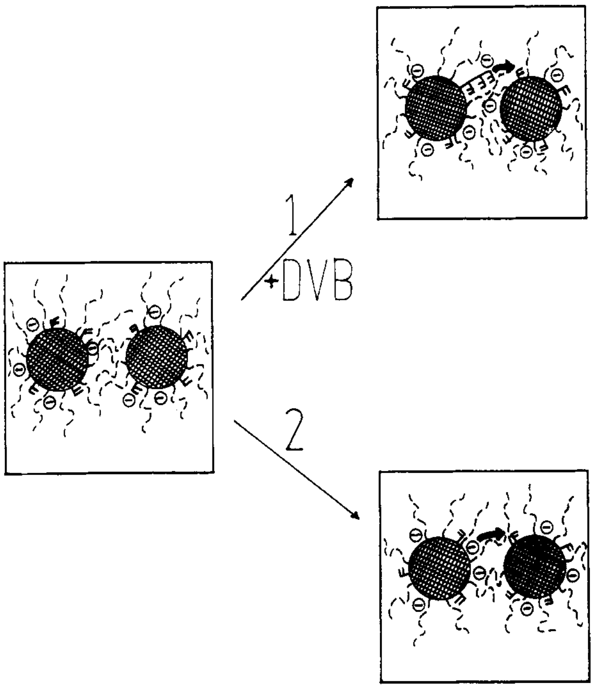

Figure 6. Two models for the agglomeration of the primary nuclei: (1) bridge formation between the particles; (2) direct contacts of the nuclei surfaces.

According to the reaction mechanism proposed above, the phase separation during the DVB polymerization takes place at a fixed length ratio of PVS insoluble to PtBS soluble blocks, regardless of their individual lengths. After the phase separation, the number of junctions between the PVS blocks of the microgel nuclei increases abruptly due to the high local concentration of polymer chains and pendant vinyl groups in the nuclei. This results in the vitrification of the microgel nuclei and, therefore, in the cessation of the polymerization and cross-linking reactions within the nuclei. Accordingly, the length ratio of PVS to PtBS blocks at cmc (r_{cmc}) together with the initial degree of swelling of PVS blocks with the DVB monomer determines the DVB content of the microgels. Thus, a further increase in the nuclei fraction of the final microgels can be achieved with increasing the value of r_{cmc}, i.e., with decreasing the initial monomer concentration of the reaction system or with increasing the swelling capacity of the nuclei using dilution of the DVB monomer with styrene.

Surface Coverage. If we assume a spherical form for the nuclei and no entanglements between the outer shell of PtBS chains and the highly cross-linked nuclei, the diameter and the surface area of the nuclei in heptane (D_{nuclei} and S_{nuclei}, respectively) can be calculated as

$$D_{\mathrm{nuclei}} = (6M_{\mathrm{w,nuclei}}/\pi N_{\mathrm{A}} d_{\mathrm{nuclei}})^{1/3} \quad (3)$$

$$S_{\mathrm{nuclei}} = \pi D_{\mathrm{nuclei}}^{2} \quad (4)$$

where N_{A} is Avogadro's number and d_{nuclei} is the density of the nuclei in heptane taken as[30] 1.0 g/cm^3.

The average distance between the bonding units of the solvated chains at the surface of the nuclei (l) can thus be calculated as

$$l = (S_{\mathrm{nuclei}}/Q)^{1/2} \quad (5)$$

The values D_{nuclei}, S_{nuclei}, and l calculated for some of the samples are given in Table III. It can be seen that up to the transition region from microgel to macrogel, the distance between two solvated chains at the nuclei surface does not change with increasing DVB concentra-

Table III
Molecular Dimensions and Surface Coverage of the Microgel Nuclei in *n*-Heptane[a]

sample	D_{nuclei}, nm	S_{nuclei}, nm^2	l, nm	$\langle r^2\rangle^{1/2}$, nm
1A	2.8	25	1.26	3.5
2A	5.6	104	1.23	3.4
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3A	23.9	1794	0.62	3.1
4A	22.3	1564	0.75	3.3
1B	3.7	44	1.48	4.3
2B	5.4	93	1.47	4.3
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6B	14.2	632	1.10	3.8
7B	18.0	1022	1.07	4.1
1C	4.2	56	2.09	6.9
2C	10.0	314	2.12	7.1
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3C	23.3	1709	1.42	7.7
4C	28.6	2576	1.36	7.1

[a] The hatched lines indicate the onset of microgel–macrogel transition regions. D_{nuclei} and S_{nuclei} are the diameter and the surface area of the nuclei in heptane, l is the average distance between the bonding units of PtBS chains at the nuclei surface, and $\langle r^2\rangle^{1/2}$ is the root-mean-square end to end distance of free PtBS chains in heptane.

tion. The values of l calculated vary between 1.2 and 2.1 nm depending on the molecular weight of PtBS and on the DVB content of the microgels. They decrease however abruptly at the transition region, probably due to the overlapping of the outer shells of the microgels in the agglomerates.

In order to compare these results with the molecular dimensions of free PtBS chains, the unperturbed dimensions parameter K_θ given by[31]

$$K_\theta = \Phi(\langle r^2\rangle_0/\bar{M}_{\mathrm{w}})^{3/2} \qquad (6)$$

was used. In eq 6 Φ is a universal constant and $\langle r^2\rangle_0$ is the mean-square end to end distance of the polymer chains at the unperturbed state. Since the molecular expansion factor, α, of polymers in the range of low molecular weight approaches unity,[32-34] the value of $\langle r^2\rangle_0$ can be taken as $\langle r^2\rangle$ of the PtBS chains in *n*-heptane. Taking $\Phi = 2.5 \times 10^{21}$ and K_θ[35,36] $= 5.42 \times 10^{-4}$ dL/g, the root-mean-square end to end distances of free PtBS chains in *n*-heptane ($\langle r^2\rangle^{1/2}$) were calculated and are given in the last column of Table III.

It seems that the distance between two chains attached at the nuclei surface is approximately $^1/_3$ of their $\langle r^2\rangle^{1/2}$ values in *n*-heptane. Thus the chains are packed close together at the surface of the highly cross-linked nuclei.

Conclusions. Previous studies of our group demonstrated that homogeneous anionic polymerization of 1,4-DVB in dilute solutions in contrast to 1,3-DVB leads to the formation of linear to weakly branched PVS chains.[37] Furthermore, anionic polymerization reactions carried out in solvent–nonsolvent mixtures resulted in the formation of insoluble macrogel particles.[25] The results presented in this study show that highly cross-linked 1,4-DVB microgels surrounded by a shell of PtBS chains can be prepared by the anionic dispersion polymerization in *n*-heptane. Thus, living PtBS chains can be used effectively in the microgel synthesis as an initiator of the DVB polymerization and also as steric stabilizers of the phase-separated particles.

The experimental results can be explained with a reaction mechanism which consists of three stages: (1) DVB polymerization in a homogeneous solution up to the critical micelle concentration of PtBS–PVS block copolymers formed, (2) fast polymerization and cross-linking reactions within the microgel nuclei, and (3) polymerization at the nuclei surface leading to interparticular reactions.

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References and Notes

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Registry No. tBS (homopolymer), 26009-55-2; PtBS (block copolymer), 126296-78-4; PtBS, 1746-23-2; 1,4-DVB, 105-06-6.