Steric stabilization of reactive microgels from 1,4-divinylbenzene

Oğuz Okay[a], *Werner Funke*

II. Institut für Technische Chemie der Universität Stuttgart, Pfaffenwaldring 55,
D-7000 Stuttgart 80, FRG

(Date of receipt: June 22, 1990)

Introduction

Reactive microgels are intramolecularly crosslinked macromolecules of colloidal sizes[1]. They can be used as multifunctional crosslinkers to form inhomogeneous networks[2], as carriers for enzymes[3], and as additives for coating systems[4]. A drawback of reactive microgels is their instability due to the pendant double bonds at the surface, which may react easily with each other to form insoluble agglomerates.

Recent studies from this laboratory have described a new method for the synthesis of reactive microgels from 1,4-divinylbenzene (1,4-DVB)[5]. The method is a non-aqueous dispersion polymerization using "living" soluble polymer chains[6]. In this method, the polymerization of 1,4-DVB is initiated by "living" poly(4-*tert*-butylstyrene) (PtBS) chains in heptane, which is a solvent for PtBS but a non-solvent for polystyrene or poly(DVB). The process results in the formation of reactive 1,4-DVB microgels surrounded and sterically protected by the PtBS chains, which are closely packed on the surface of the microgel nuclei[5]. Fig. 1 shows the schematic representation of a microgel particle in heptane. Reactive microgels containing up to 30–35% nuclei (crosslinked poly(DVB)) were prepared using this method. A further increase in the DVB concentration led to the formation of insoluble macrogel particles, regardless of the length of the PtBS chains[5]. Recently, Rempp et al. have also synthesized reactive microgels with a similar structure, however, they used the homogeneous anionic polymerization technique[7].

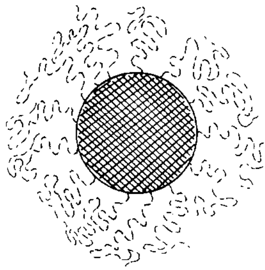

Fig. 1. Schematic representation of a microgel particle in heptane illustrating the PtBS chains and the microgel nucleus. We assume an ideal spherical form for the nuclei and no entanglements between the outer shell of PtBS chains and the nuclei

In the present article, we demonstrate the stabilizing effect of the solvated PtBS chains against the agglomeration of microgel particles. For this purpose, the molecular

---

[a] Permanent address: Eastern Mediterranean University, Department of Chemistry, Gazimagusa, T.R.N.C., Mersin 10, Turkey.

CCC 0173-2803/90/$01.00

weight of the microgels and their particle size distribution were investigated as a function of reaction time, by light scattering techniques. The monomer conversion was determined by UV spectrophotometry.

Experimental part

Materials: 4-*tert*-Butylstyrene was prepared from 4-*tert*-butylbenzene as described in ref.[8,9]. Purity was checked by gas chromatography (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[10]. 1,4-DVB was then further purified by crystallization from methanol[5]. Its purity was 96%. Heptane (Merck, p. a.) was used as the solvent after further purifications[5]. *sec*-Butyllithium (*sec*-BuLi, Aldrich) as a 12 wt.-% solution in cyclohexane/isopentane mixture was used without further treatment. Its concentration was determined by the Gilman-Haubein double titration method[11].

Polymerization: All experiments were carried out under purified nitrogen[*]. The experimental set-up and procedures used for anionic polymerization were identical with those described previously[5]. "Living" PtBS chains were prepared in heptane with *sec*-BuLi at 50 °C and at a monomer concentration of 5 wt.-%. The reaction was complete after 3 h. A small amount of the heptane solution was then removed from the reactor and used for molecular weight determination of the living PtBS chains thus obtained. The number-average molar mass of living PtBS ranged from 3500 to 4200 $g \cdot mol^{-1}$. To the heptane solution of the living PtBS, at 50 °C, a 1,4-DVB solution in heptane was added dropwise, within 3 min, under vigorous stirring. The polymerization was then continued for 4 h at 50 °C; small samples were removed from the reactor during this time to characterize the polymers formed and to determine the monomer conversion. The initial DVB concentration used was kept constant close to the microgel-macrogel transition region[5], i. e., the final microgels contained 34% crosslinked 1,4-DVB nuclei.

Characterization: The number-average molar mass ($\overline{M}_n$) of PtBS was measured in toluene at 61 °C using a Knauer vapor pressure osmometer. The weight-average molar mass of the microgels ($\overline{M}_w$) was determined by small angle light scattering (Chromatix KMX-6) at 25 °C with a laser light source at 633 nm. Cyclohexane was used as the solvent of the microgel samples[5]. The refractive index increments (dn/dc) were measured with a Chromatix KMX-16 differential refractometer. Quasi-elastic light scattering experiments were performed using a PCS 100 spectrometer and a K7027 "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 heptane and at a polymer concentration of about 0,2 wt.-%. The scattering angle was 90°. The data were analysed and the particle size distribution of the samples was calculated using the exponential sampling method (Autosizer II). The UV spectroscopic measurements were carried out using a Perkin-Elmer spectrometer (Lamda 15 UV/VIS). The absorption maximum, at 310 nm, of the unreacted 1,4-DVB monomer in the terminated reaction mixture was used to calculate the monomer conversion. A linear calibration curve (length of the absorption band at 310 nm versus 1,4-DVB concentration) was prepared using terminated PtBS solutions containing a known content of 1,4-DVB monomer.

Results and discussion

During the divinyl monomer polymerization in dilute solution and with a low-molecular-weight initiator, the molecular dimensions of the polymers are known to

---

[*] Argon could be more suitable than nitrogen in the experiments. Indeed, we found that in the case of unbranched BuLi the molar mass of PtBS deviated considerably from the calculated value. For *sec*-BuLi, however, both the experimental and calculated molar masses matched close together.

increase at first slowly as a result of the formation of the microgel particles[12-15]. As the reaction proceeds, the abrupt increase in the molecular dimensions is due to agglomeration phenomena. The pendant double bonds located at the surface of the microgel are responsible of the formation of insoluble agglomerates. In Fig. 2, the dashed curve illustrates a typical dependence of the weight-average molar mass ($\overline{M}_w$) on reaction time for such polymers, which we shall call thereafter "unprotected microgels". The circles in Fig. 2 represent the results of our measurements on "protected" microgels. The solid curve is the best fit to experimental data, which shows the change in $\overline{M}_w$ of the microgels as a function of reaction time. The change in the values of $\overline{M}_w$ is rapid in the first period of time up to 45 min, and it keeps slightly increasing with increasing reaction time (Fig. 2 and Tab. 1). A comparison of the curves in Fig. 2 indicates that the rate of the agglomeration reactions is significantly reduced by PtBS chains on the nuclei surface.

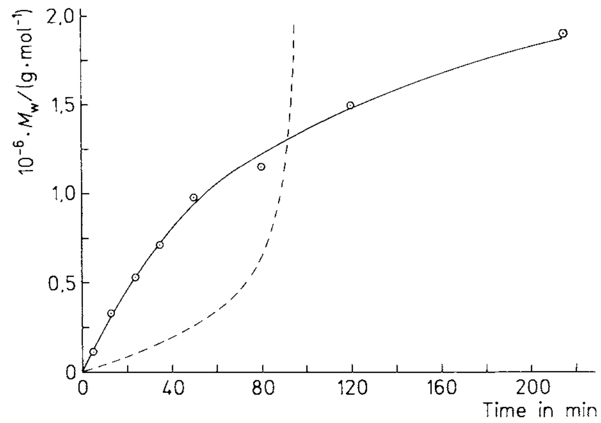

Fig. 2. Dependence of the weight-average molar mass of the microgels $\overline{M}_w$ on reaction time. The dashed curve illustrates the same dependence in an arbitrary time scale for unprotected microgels

The particle size distribution of the microgels in heptane is given in Fig. 3 for various reaction times. It can be seen that the number of particles with diameters ranging from

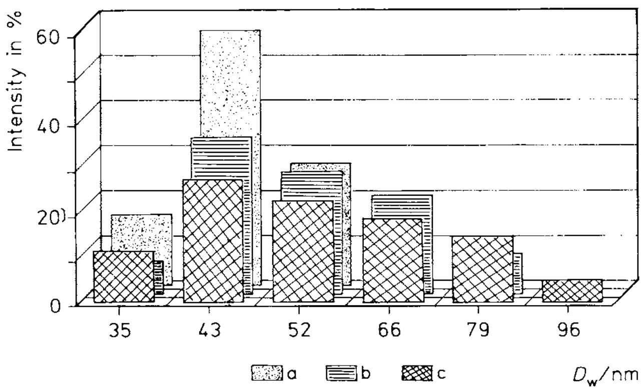

Fig. 3. Particle size distribution (by intensity) of the microgels in heptane. The reaction times for their synthesis are 25 (a), 50 (b) and 210 min (c)

35 to 50 nm decreases with increasing reaction time and that new particles with diameters of 60 to 80 nm are formed. Longer reaction times up to 210 min lead to no significant changes in the particle diameters. These results also indicate that the PtBS chains are effective stabilizers for 1,4-DVB microgel particles dispersed in heptane.

Fig. 4 shows the spectra of terminated polymer mixtures at various reaction times. The unreacted 1,4-DVB monomer has an absorption maximum at 310 nm. The absorption band at 294 nm is attributed to the pendant vinyls on the polymer backbone, resulting from reaction of one of the vinyl groups of the DVB monomer[16,17]. The DVB conversion was calculated from the recorded decrease of the absorption at 310 nm and is given in Tab. 1. The 1,4-DVB monomer converts to the polymer very rapidly and

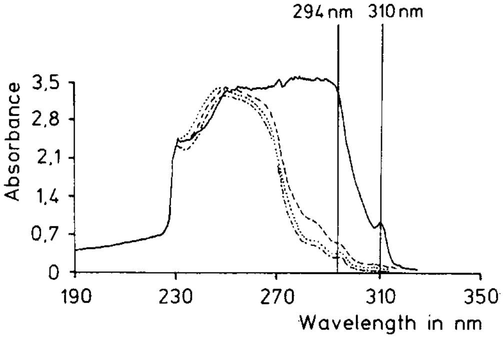

Fig. 4. The UV spectra of terminated and diluted reaction mixtures in heptane. The reaction times are 0,3 (————), 5 (– – –), 17 (. . . . .) and ⩾ 30 min (–.–.–)

Tab. 1. Characteristics of the polymer samples and monomer conversions in the course of the 1,4-DVB polymerization using "living" PtBS chains in heptane[a)]

Reaction time in min	$\frac{10^{-3}\cdot\overline{M}_w}{g\cdot mol^{-1}}$	Conv. in mol-%	PV
0[b)]	3,5–4,2[c)]	0	
0,3	—	13	
5	113	90	
13	330	—	
17	—	94	
24	530	—	
30	—	100	0,32
35	714		
50	980		0,30
80	1 150		
120	1 500		
215	1 900		0,33

[a)] $\overline{M}_w$ is the weight-average molar mass of the microgels, conv. is the conversion of 1,4-DVB monomer and PV is the fraction of DVB units in the polymer with pendant double bonds.

[b)] Onset of the 1,4-DVB addition of the reaction mixture.

[c)] Number-average molar mass of living PtBS chains.

the conversion levels off after 17–30 min. The amount of pendant vinyl groups also decreases rapidly (Fig. 4) but attains an almost constant value after 30 min. The residual unsaturations determined by IR spectroscopy[15] amount to 0,30–0,33 (fraction of DVB units with pendant vinyl groups) (Tab. 1).

We can conclude that polymerization and crosslinking reactions take place in the first 30 min of the reaction. During this stage of the reaction the molecular weight and the particle size of the polymers increase and their pendant vinyl group content decreases. At the end of this stage, all of the monomer is consumed, and 67 to 70% of the monomer is incorporated into the polymer via both vinyl groups, which points to the formation of highly cross-linked microgel particles. Contrary to what was observed with unprotected microgels, longer reaction times lead to insignificant changes in the molecular dimensions of the microgel particles: they are stable against agglomeration even in their highly reactive ionic forms. It may be concluded that the synthesis of reactive microgels with a protective layer at the surface may provide an extension of the applications of unprotected microgels. It is interesting to apply this method to other reactive microgels, i.e., those from ethylene dimethacrylate.

We are indebted to *Alexander von Humboldt-Stiftung* for a grand to Oğuz Okay and to the *Deutsche Forschungsgemeinschaft e. V.* for supporting these studies.

[1] For a recent review, see: W. Funke, *Br. Polym. J.* **21**, 107 (1989)
[2] W. Funke, *Chimia* **22**, 111 (1968)
[3] U. Seitz, H. E. Pauly, *Angew. Makromol. Chem.* **76/77**, 315 (1979)
[4] A. J. Backhouse, *J. Coat. Technol.* **54**, 83 (1982)
[5] O. Okay, W. Funke, *Macromolecules* **23**, 2623 (1990)
[6] K. E. J. Barrett, *"Dispersion Polymerization in Organic Media"*, Wiley, New York 1975
[7] F. A. Taromi, P. Rempp, *Makromol. Chem.* **190**, 1791 (1989)
[8] J. C. Butler, L. L. Ferstandig, R. D. Clark, *J. Am. Chem. Soc.* **76**, 1906 (1954)
[9] L. L. Ferstandig, J. C. Butler, A. E. Straus, *J. Am. Chem. Soc.* **76**, 5779 (1954)
[10] R. H. Wiley, J. I. Jin, Y. Kamath, *J. Polym. Sci., Part A-1* **6**, 1065 (1968)
[11] H. Gilman, A. H. Haubein, *J. Am. Chem. Soc.* **66**, 1515 (1944)
[12] W. Straehle, W. Funke, *Makromol. Chem.* **179**, 2145 (1978)
[13] H. Kast, W. Funke, *Makromol. Chem.* **180**, 1335 (1979)
[14] H. Galina, K. Dusek, Z. Tuzar, M. Bohdanecky, J. Stokr, *Eur. Polym. J.* **16**, 1043 (1980)
[15] J. Kaczun, Diplomarbeit, University of Stuttgart, 1989
[16] D. J. Worsfold, *Macromolecules* **3**, 514 (1970)
[17] T. Batzilla, Thesis, University of Stuttgart, 1988