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Studies on microgels. 5. Synthesis of microgels via living free radical polymerisation

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Abstract

Statistical and star microgels of *t*-butylstyrene-1,4-divinylbenzene (TBS-DVB) have been synthesized via living free radical polymerization using tetramethylpiperidin-1-oxyl (TEMPO) as a trapping agent. The alkoxyamines **1** and **2** were used as initiators to prepare statistical and star microgels, respectively. The molecular weight of the resulting microgels was determined by size exclusion chromatography with an on-line multi-angle laser light scattering (MALLS) instrument. It has been found that living free radical polymerization provides a much better control over the formation of statistical microgels than traditional free radical polymerization and can be used successfully for the synthesis of star microgels. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Statistical microgels; Star microgels; Characterization

1. Introduction

Microgels can be defined as intramolecularly crosslinked, high molecular weight soluble polymers and were first described by Staudinger and Husemann [1]. They found that the free radical polymerization of dilute solutions of divinyl or vinyl/divinyl monomers led initially to the formation of macromolecules with pendant vinyl groups. Depending on the reaction conditions, these vinyl groups can undergo random intramolecular/intermolecular crosslinking reactions forming statistical microgels (Fig. 1). Therefore, statistical microgels have a random distribution of crosslinks and lack structural control due to the irreversible termination steps. Various systems have been studied including styrene/1,4-divinyl benzene (DVB) [2–5].

Alternatively, star microgels are characterized by a very high degree of structural control. Typically star microgels are composed of a series of linear arms held together by a central crosslinked core (Fig. 1). They are generally prepared via anionic polymerization, relying on the "living" nature of the polymer chain for the introduction of the crosslinker [6,7].

Solomon et al. [8] first reported the process based on alkoxyamines/nitroxides known as living free radical polymerization. Since then, it has been employed by different authors [9–11] to synthesize well-defined linear and block copolymers of low polydispersity. This technique utilizes a stable free radical such as nitroxyl radicals as the trapping agent. These radicals combine with the propagating radicals and form a labile bond, which can undergo reversible homolytic dissociation at higher temperatures.

We have previously briefly described a new technique for the formation of microgels by living free radical polymerization [12]. We now report the full detail of this methodology to synthesize both statistical and star microgels using *t*-butyl styrene (TBS)/DVB monomers, the influence of reaction conditions and the characterization of these new materials.

2. Experimental

2.1. Materials

All chemicals were obtained from Aldrich. TBS was distilled prior to reaction. Purification of DVB was carried out by the method of Wiley [13]. Tetramethylpiperidin-1-oxyl (TEMPO) radical was used without further purification. Benzene was refluxed over sodium for 16 h and then distilled prior to use.

2.2. Polymerization

The aminoxy terminated initiators **1** and **2** (Fig. 2) were synthesized as we previously described [12]. The chain

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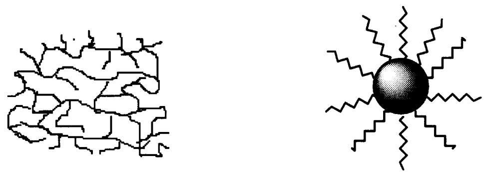


Statistical Microgels

Star Microgels

Fig. 1. Schematic representation of statistical and star microgels.

growth capability of initiator **1** to produce linear, well-defined poly(TBS) was examined by making a series of polymers as a function of time and that of initiator **2** was synthesized by such chain extension polymerization. The formation of statistical and star microgels was studied as a function of time and feed ratio of monomers.

2.2.1. Preparation of linear poly(TBS) using alkoxyamine 1

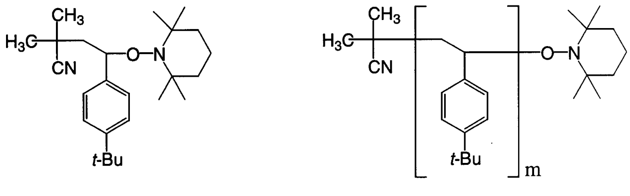
TBS (0.960 g, 6.00 mmol) and alkoxyamine **1** (0.025 g, 0.065 mmol) were dissolved in benzene (1.2 ml) and degassed via three freeze–pump–thaw cycles. The mixture was then sealed under vacuum and heated at 130°C for varying reaction times. The resulting polymer alkoxyamine **2** was precipitated from methanol to afford a white powder (Table 1, Ptbsr1–Ptbsr5).

2.2.2. Chain extension reaction of alkoxyamine 2

A solution of alkoxyamine **2** (Ptbsr6) (0.100 g, 0.03 mmol) and TBS (0.175 g, 1.10 mmol) in benzene (1.0 ml) was degassed via three freeze–pump–thaw cycles, sealed under vacuum and heated at 130°C for 21 h. The resulting polymer was precipitated from methanol (Table 1, Ptbstbs).

2.2.3. Preparation of statistical microgels

A solution of alkoxyamine **1** (0.025 g, 0.066 mmol), TBS (1.120 g, 7.0 mmol) and DVB (0.390 g, 3.0 mmol) in benzene (7.6 ml) was degassed via three freeze–pump–thaw cycles, sealed under vacuum and heated at 130°C for varying reaction times. The resulting statistical microgel was precipitated from methanol as a white powder. The same procedure was followed for reactions with various TBS/DVB ratios (Table 2).



1

2

Fig. 2. Monomeric and polymeric alkoxyamine terminated initiators.

Table 1
Properties of linear alkoxyamine terminated poly(TBS) as a function of reaction time ([alkoxyamine **1**] = 0.054 M, [TBS] = 5 M)

Sample[a]	Time (h)	Molecular weight[b]		PD	Yield (%)
		$M_n \times 10^{-3}$	$M_w \times 10^{-3}$		
Ptbsr1	6	5.52	6.05	1.09	37
Ptbsr2	17	5.90	6.67	1.13	46
Ptbsr3	24	7.54	8.48	1.12	50
Ptbsr4	48	9.14	10.64	1.16	69
Ptbsr5	72	9.44	11.22	1.18	79
Ptbsr6[c]	–	3.28	3.61	1.10	–
Ptbstbs	21	6.93	7.70	1.11	–

[a] Ptbsr denotes alkoxyamine terminated poly(TBS) linear polymer.
[b] SEC-DRI relative to polystyrene standards (g/mol).
[c] [Ptbstb6] = 0.03 M, [TBS] = 1.10 M.

2.2.4. Preparation of star microgels

Star microgels were prepared by a similar procedure, where polymeric initiator alkoxyamine **2** was used. The central crosslinked core of the resulting star microgel was either formed by polymerizing varying amounts of DVB only in the feed mixture (Table 3) or a mixture of TBS and DVB (Table 4) under different reaction times.

Both microgel samples were precipitated from methanol, filtered and dried under vacuum. All the microgel synthesis reactions were carried out in 20% benzene solution.

2.3. Instrumentation

Size exclusion chromatography (SEC) was carried out using a Waters 510 HPLC pump in conjunction with the Wyatt Technology Dawn F multi-angle laser light scattering (MALLS) instrument and the Waters 410 differential refractometer (DRI) as on-line detectors. Wyatt Technology ASTRA and EASI software and Waters BASELINE packages were used for data collection and analysis. A set of Waters ultrastyragel columns (10^5, HR2 and HR4) was used for the separation of the polymers using HPLC grade THF at a flow rate of 1.0 ml/min. The polydispersity, PD = M_w/M_n, where M_w and M_n are the weight average and number average molecular weights, respectively.

3. Results and discussion

3.1. Synthesis of linear polymer arms

The polymerization of TBS using a living free radical technique was carried out to examine the performance of initiator **1** under the conditions to be used for the microgel synthesis. Linear aminoxy terminated poly(TBS) polymers were prepared using alkoxyamine **1** as a function of reaction time. The samples were analyzed by SEC-DRI for molecular weight properties and the yield determined (Table 1). It was observed that both the molecular weight and the yield increased as a function of reaction time, which is indicative

Table 2
Reaction conditions and properties of statistical microgels

Sample[a]	TBS/DVB[b]	Time (h)	Yield (%)	$M_w \times 10^{-5}$ (g/mol)		d*n*/d*c*[c]
				DRI	MALLS	
Ptbsdvr1	70:30	24	38	0.42	2.13	0.178
Ptbsdvr2	70:30	48	44	0.59	4.75	0.179
Ptbsdvr3	70:30	72	48	0.72	7.60	0.181
Ptbsdvr4	80:20	72	49	1.15	3.80	0.172
Ptbsdvr5	90:10	72	49	0.55	1.47	0.165

[a] Ptbsdvr denotes statistical microgel.
[b] Feed ratio.
[c] Refractive index increment.

of a living free radical polymerization mechanism. In addition, the fact that the polydispersity consistently remained low was further evidence that the reaction proceeded in a controlled fashion and that the thermal polymerization of TBS without capping with TEMPO in the chain end is not significant under these reaction conditions.

The chain extension reaction of polymeric alkoxyamine **2** in the presence of TBS resulted in a polymer of increased molecular weight and the narrow molecular weight distribution remained (Table 1, Ptbstbs). The chromatograms (Fig. 3) show that almost all the polymer chains participated in the chain extension reaction. It also demonstrates that TEMPO terminated polymer chains have the potential to act as precursors for the synthesis of well-defined, narrow polydispersity polymers with different architecture. This concept was subsequently used to synthesize microgels by living free radical polymerization.

3.2. Microgel: synthesis and characterization

Microgels can be synthesized by polymerizing divinyl or monovinyl/divinyl monomers. In the case of anionic polymerization of DVB, polymer chains with pendent double bonds are formed due to the large difference in reactivity of the two double bonds. It is reported that the reactivity of the first double bond is approximately 10 times higher than that of the second double bond under anionic conditions [6]. These pendent vinyl groups can undergo intra- or intermolecular crosslinking reactions. In free radical polymerization, the reactivity of two double bonds of DVB is approximately equal. Therefore, the incorporation of both double bonds into the polymer chains during the polymerization reaction take place simultaneously.

3.2.1. Statistical microgels

Statistical microgels were prepared by a standard one-pot procedure similar to traditional free radical microgels. In this polymerization, alkoxyamine **1** was used as initiator instead of for example AIBN, which is often used during free radical microgel formation. Microgel synthesis using AIBN requires highly dilute solutions in order to avoid macrogel formation and attempts to prepare microgels using AIBN at the concentrations used for alkoxyamine **1** gave extensive gelation. The results of microgel formation under living free radical conditions are shown in Table 2. The molecular weight of the microgels increased as a function of reaction time (Table 2, Ptbsdvr1–Ptbsdvr3). The SEC chromatograms of the samples Ptbsdvr1–Ptbsdvr3 (Fig. 4a) showed the formation of three types of microgel particle under the experimental conditions. These results are surprising as one may predict that such formed microgels might only have one type of particle with a broad distribution. Closer examination of the SEC chromatograms revealed that the difference in the elution volume of each peak maxima in the curve is approximately the same. This may indicate that the higher molecular weight microgel

Table 3
Reaction conditions and properties of star microgels with DVB central core (reaction conditions: benzene (7.6 ml), temperature = 130°C for 48 h; arms: polymeric alkoxyamine **2** (Ptbsr7) ($M_w = 5454$, PD = 1.15, 0.300 g))

Sample[a]	DVB[b]	Yield (%)	$M_w \times 10^{-5}$ (g/mol)		d*n*/d*c*
			DRI	MALLS	
Ptbsdvrs1	1.68	71	0.75	2.20	0.177
Ptbsdvrs2	1.26	78	0.38	0.59	0.174
Ptbsdvrs3	0.84	84	0.32	0.37	0.161

[a] Ptbsdvrs denotes star microgel samples.
[b] Amount of DVB in feed (mmol).

Table 4
Reaction conditions and properties of star microgels with DVB/TBS copolymer central core (reaction conditions: benzene (7.6 ml), TBS/DVB feed ratio 70:30, DVD (0.329 g, 2.53 mmol), TBS (0.963 g, 6.00 mmol), temperature = 130°C; arms: polymeric alkoxyamine **2** (Ptbsr8) ($M_w = 2954$, PD = 1.09, 0.150 g))

Sample[a]	Time (h)	Yield (%)	$M_w \times 10^{-5}$ (g/mol)		d*n*/d*c*
			DRI	MALLS	
Ptbsdvrs4	24	35	0.15	0.88	0.180
Ptbsdvrs5	48	40	0.22	2.08	0.176
Ptbsdvrs6	72	46	0.31	2.33	0.184

[a] Ptbsdvrs denotes star microgel samples.

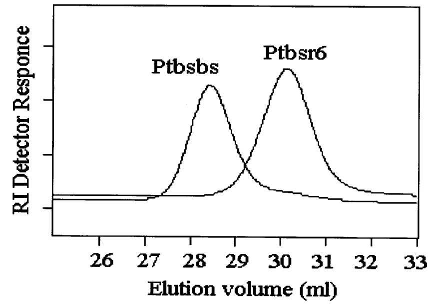


Fig. 3. Chain extension polymerization of alkoxyamine terminated poly(TBS).

particles are formed through the aggregation of smaller molecular weight particles via some form of interparticle crosslinking reaction. SEC-DRI chromatograms also showed that the majority of microgel particles are of high molecular weight, i.e. mainly highly crosslinked particles. This observation is in agreement with the chromatograms recorded using the light scattering detectors (SEC-MALLS). Fig. 4b shows the SEC-MALLS trace of Ptbsdvr3, and it is noted that the low molecular weight polymeric species do not appear very obviously. This is due to the intensity of the light scattering signal being proportional to the molecular weight and sample concentration. The microgel particles with the lower molecular weight observed in the SEC-DRI trace are more prominent as its detector response is proportional to the concentration of the polymer only. The d*n*/d*c* values of these microgels as determined from SEC-MALLS showed that these values changed very little with reaction time.

For a given reaction time, as the concentration of the DVB was decreased in the feed ratio, the molecular weight of the resulting microgels also decreased (Table 2, Ptbsdvr3–Ptbsdvr5). This is consistent with the fact that the smaller number of DVB molecules available limits the chance of crosslinking. Correspondingly, the d*n*/d*c* value determined by SEC-MALLS also lowered as the concentration of DVB in the system was reduced.

For the SEC-DRI measurements, polystyrene standards were used for the calibration, as there are no standards available with a similar structure of microgels. Therefore, the molecular weights produced from such measurements are relative and only used for comparison among the samples. On the other hand, SEC-MALLS measurements are an absolute method and capable of accurately determining the molecular weight without the need for standards. Therefore, the real molecular weight of these microgels should be quoted from these measurements.

3.2.2. Star microgels

Previously star microgels have been synthesized by anionic or group transfer polymerization methods. Traditional free radical polymerization methods are not suitable for such synthesis, as there is no controlled end to facilitate the formation of such molecular architecture. Living free radical polymerization results in the formation of nitroxide terminated polymer chains, which could undergo further polymerization if the same monomer is used in the chain extension reaction or can initiate the crosslinking reaction if a crosslinker is introduced. Therefore, it should be possible to synthesize star microgels using controlled free radical polymerization.

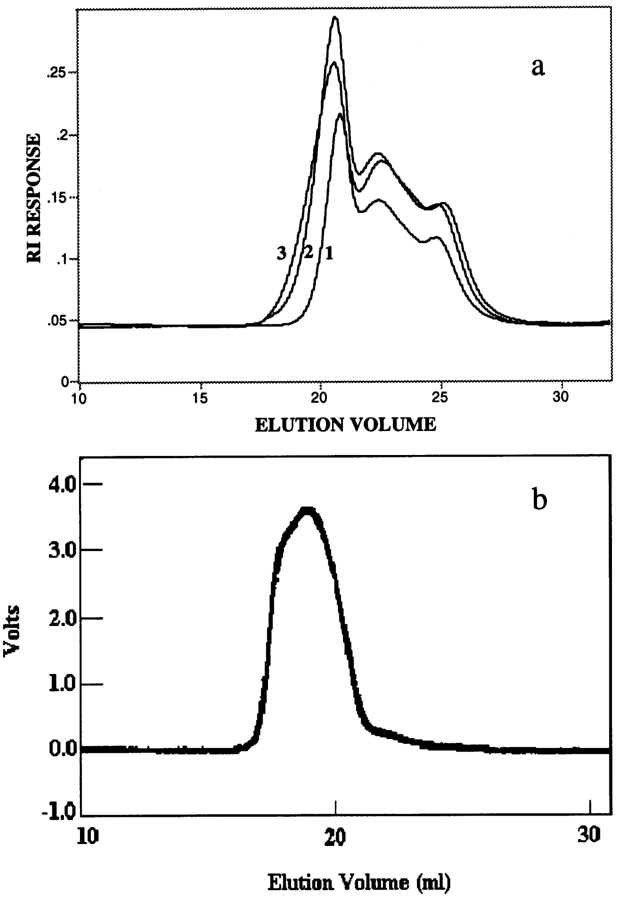


Fig. 4. (a) SEC-DRI traces of statistical microgel samples (1 = Ptbsdvr1, 2 = Ptbsdvr2 and 3 = Ptbsdvr3); (b) SEC-MALLS traces (90°C) of statistical microgel sample Ptbsdvr3.

Two approaches were used to synthesize such star microgels. In the first, polymerizing DVB with the alkoxyamine **2** as linear arms (Table 3) formed the central core. As there is only one potentially active chain end on the alkoxyamine **2**, reaction can only occur from this end with DVB. Consequently, the crosslinked DVB core will link alkoxyamine **2** on one end forming linear arms (Fig. 1). Reactions were carried out on preformed arms (M_w 5454 g/mol, PD 1.15) and varying the amount of DVB added. When the amount of DVB used was reduced to half (Ptbsdvrs1 to Ptbsdvrs3), the M_w of the resulting microgel reduced more than 80%. The value of the d*n*/d*c* was also reduced from 0.177 to 0.161.

The SEC-DRI chromatograms of these microgels showed the formation of two types of species (Fig. 5). The peak at high elution volume is very close to the peak that

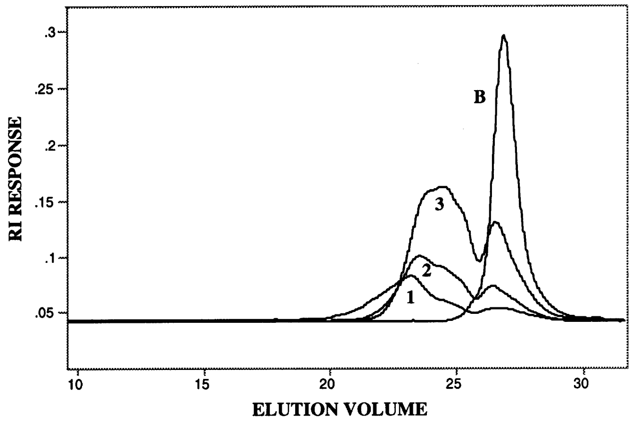


Fig. 5. SEC-DRI traces of star microgels with DVB central core (1 = Ptbsdvrs1, 2 = Ptbsdvrs2, 3 = Ptbsdvrs3 and B = Ptbsr7).

corresponds to the arms used (Ptbsr7). This may be due to the crosslinking of a few alkoxyamine **2** by the DVB used. The majority of the sample consists of high molecular weight polymer in all cases. The molecular weight of the microgels increased and the peak molecular weight shifted to a lower elution volume with increasing DVB content in the feed ratio. The light scattering trace of microgel sample Ptbsdvrs3 was similar to the one observed in statistical microgels and mainly contained high molecular weight particles. The low molecular weight particles only appear as a shoulder in the 90° trace.

The other approach taken was to synthesize the central core by polymerizing a DVB/TBS mixture (Table 4). The weight average (M_w) of the arms used was 2954 g/mol, the feed ratio of DVB/TBS was kept constant and the reaction was carried out for different time intervals. The molecular weight of the microgels increased with reaction time (Fig. 6), which is clearly shown in the SEC chromatograms; almost all the alkoxyamine terminated polymeric chains participated in the microgel formation. The concentration of high molecular weight particles increased with reaction time. The formation of different peaks as shown in the SEC chromatogram is similar to what was observed in the statistical microgel synthesis. In this case, the microgel particles seem to undergo interparticle linkage to yield high molecular weight microgels. The light scattering chromatograms of these microgels were similar to the samples from the first approach and only showed high molecular weight microgel particles.

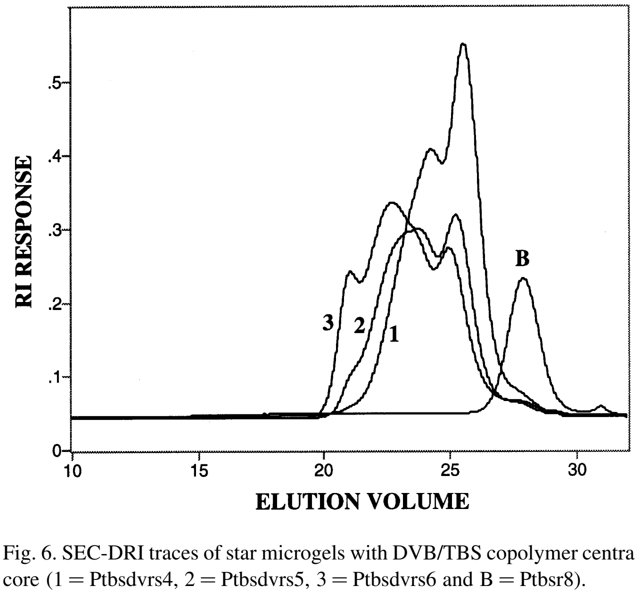


Fig. 6. SEC-DRI traces of star microgels with DVB/TBS copolymer central core (1 = Ptbsdvrs4, 2 = Ptbsdvrs5, 3 = Ptbsdvrs6 and B = Ptbsr8).

Compared to the microgels produced from the first approach, with a DVB core only, the molecular weight of the microgels formed with DVB/TBS copolymer core were higher on average. This may be due to the relatively lower density core having a bigger size and being able therefore to accommodate more arms.

4. Conclusion

The nitroxide mediated free radical polymerization has successfully been applied to the synthesis of statistical and star microgels. This new methodology overcomes the problem of gelation associated with the polymerization of divinyl monomers by traditional free radical processes for the synthesis of statistical microgels. It provides better control of molecular weight properties of the polymers and is applicable to solutions with much higher divinyl monomer concentration. The formation of star microgels was possible with this technique. The chemistry presented has hence provided enormous potential to use other monomers to synthesize microgels with different properties.

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