polymer

Polymer 40 (1999) 6583–6589

Studies on microgels[☆]
4. The effect of solvent on the synthesis of *t*-butylstyrene-divinylbenzene microgels by anionic polymerization

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Received 14 September 1998; received in revised form 4 January 1999; accepted 5 January 1999

Abstract

t-Butylstyrene-1,4-divinylbenzene (TBS-DVB) microgels were synthesized by the arm first living anionic polymerization technique using two different solvents, heptane, a good solvent for poly(TBS) arms only and tetrahydrofuran (THF), a good solvent for both the arms and the poly(*t*-butylstyrene-co-4-vinylstyrene) block copolymer formed initially before crosslinking. The polymerizations were carried out using *t*-butyllithium as an initiator. The resulting microgels were characterised by size exclusion chromatography with an on-line multi angle laser light scattering instrument. In the polar solvent THF, much better control of the molecular weight of the microgels was observed. It is suggested that the mechanism of microgel formation is influenced by the solvent. Micelle formation is favoured in the case of heptane, which is a poor solvent for 4-vinylstyrene blocks. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymers; Microgels; Size exclusion chromatography

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1. Introduction

Microgels are defined as intramolecularly crosslinked, high molecular weight soluble polymers. Different polymerization techniques have been used to prepare microgels [1]. Star microgels have been synthesized in past years by sequential anionic polymerization of, for example monovinyl monomers such as *t*-butylstyrene [2–4] (TBS) and styrene [5–7] and a crosslinking monomer such as 1,4-divinylbenzene (DVB). *t*-Butylstyrene-divinylbenzene (TBS-DVB) microgels have been prepared in heptane using sec-butyllithium as an initiator. Heptane is a good solvent for poly(TBS) chains but a poor solvent for the poly(4-vinylstyrene) blocks. In these polymerizations, linear chains of TBS are synthesized first, followed by the addition of DVB to form a crosslinked central core that is stabilised by the linear chains. It is suggested [5] that first, a block copolymer (TBS-co-4-vinylstyrene) is formed and that these linear blocks then arrange themselves into micelles, because heptane is a good solvent for poly(TBS) chains and a poor solvent for 4-vinylstyrene blocks. The crosslinking reaction takes place within the micelles resulting in the formation of microgels. Star microgels of styrene/divinylbenzene/*t*-butylacrylate [8] and styrene/divinylbenzene/2-vinylpyridine [9] have also been reported. Alternatively, very high molecular weight divinylbenzene/styrene star microgels have been prepared using the core first method in which styrene arms are grown from a living poly(divinylbenzene) core [3].

The arm first method is preferred over the core first method because the molecular weight distribution of the resulting microgels is narrower and no gelation of the reaction medium is observed [10].

In this article, we describe the effect of a polar and of a non-polar solvent on the synthesis of (TBS-DVB) microgels and on the molecular weight distribution of poly(TBS) chains. Molecular weight distribution of the microgels is investigated as a function of reaction time in tetrahydrofuran (THF) and various feed ratios of crosslinking monomer in THF and heptane.

2. Experimental

2.1. Materials

All the chemicals were obtained from Aldrich. TBS was

[☆] Part 3: Abrol S, Kambouris PA, Looney MG, Solomon DH. Macromol. Rapid Commun. 1997;18:755.

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PII: S0032-3861(99)00019-1

Table 1
Reaction conditions for the synthesis of linear poly(TBS) arms and microgels in THF and heptane

Sample[a]	Molar feed ratio TBS:DVB	Reaction time (min.)[b]	Reaction temperature (°C)	Yield (%)	Solvent
PTBSA11	—	60	−78	—	THF
MDVBA10	70.56:29.44	210	−40	~100	THF
PTBSA15	—	60	−78	—	THF
MDVBA14	80.75:19.25	210	−40	~100	THF
PTBSA14	—	60	−78	—	THF
MDVBA13	89.82:10.18	210	−40	~100	THF
PTBSA4	—	150	50	—	Heptane
MDVBA4	70.42:29.58	150	50	~100	Heptane
PTBSA5	—	150	50	—	Heptane
MDVBA5	80.21:19.79	150	50	~100	Heptane
PTBSA6	—	150	50	—	Heptane
MDVBA6	89.82:10.18	150	50	~100	Heptane

[a] PTBSA denotes linear poly(TBS) arms for preceding microgel sample and MDVBA denotes microgel samples.

[b] Reaction time for microgel samples is time after the addition of DVB.

distilled over calcium hydride twice and stored under an argon atmosphere. 1,4-divinylbenzene (DVB) was separated from a commercially available technical mixture by the method of Wiley [11] and then distilled over calcium hydride twice and stored under an argon atmosphere. *t*-Butyllithium was used without any further purification. THF and heptane were refluxed over potassium under argon atmosphere, checked for dryness with benzophenone and distilled prior to use.

2.2. Polymerization

All the glassware and syringes were dried in a 110°C oven overnight and purged with argon before use. Polymerizations were carried out under argon atmosphere.

For a typical polymerization procedure, a two neck round bottom flask was flame dried three times under vacuum and flushed with argon each time. The required amount of freshly distilled THF was introduced into the two neck round bottom flask and the solvent was cooled to −78°C. The appropriate amount of *t*-butyllithium was added followed by the addition of TBS. The solution turned into an orange red colour indicating the start of TBS polymerization. A poly(TBS) sample was taken after 1 h for the analysis of the molecular weight distribution of the arm. The temperature of the reaction was increased to −40°C before DVB was added to the poly(*t*-butylstyryl) anion. Samples of the polymers were taken at different times to monitor the progress of the reaction. The same procedure was followed for various amounts of DVB as shown in Table 1.

In the case of heptane, the solution containing TBS was heated to 50°C and then the required amount of *t*-butyllithium was added to the reaction mixture. The

Table 2
Properties of linear poly(TBS) arms and microgels prepared in THF and heptane

Sample[a]	SEC-DRI[b]			SEC-MALLS[b]		
	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$ (g/mol)	PD[c]	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$ (g/mol)	PD[c]
PTBSA11	0.052	0.055	1.06		—	
MDVBA10	0.82	1.31	1.60	2.48	5.21	2.09
PTBSA15	0.050	0.054	1.07		—	
MDVBA14	0.45	0.53	1.18	1.26	1.63	1.29
PTBSA14	0.050	0.053	1.06		—	
MDVBA13	0.29	0.33	1.13	0.81	0.92	1.13
PTBSA4	0.072	0.123	1.70		—	
MDVBA4	1.66	2.87	1.72	12.0	36.8	3.06
PTBSA5	0.077	0.139	1.80		—	
MDVBA5	1.25	1.68	1.34	5.53	10.2	1.84
PTBSA6	0.079	0.137	1.74		—	
MDVBA6	0.81	1.02	1.26	2.14	3.56	1.66

[a] PTBSA denotes linear poly(TBS) arms for preceding microgel sample and MDVBA denotes microgel samples.

[b] SEC-DRI (SEC) and SEC-MALLS (SEC with on-line MALLS detector) were used to determine number average molecular weight (M_n) and weight average molecular weight (M_w).

[c] PD is the polydispersity (M_w/M_n).

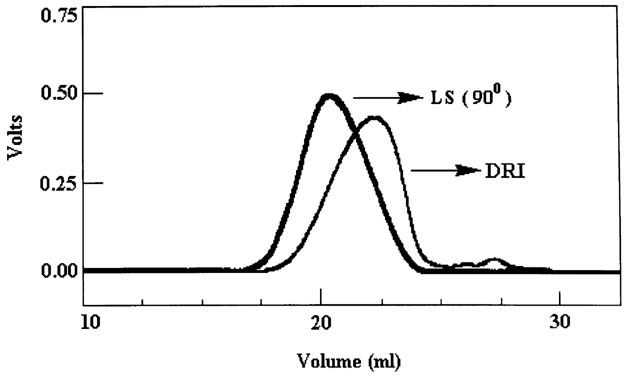

Fig. 1. SEC-DRI and SEC-MALLS traces of MDVBA10 (THF).

polymerization was carried out for 150 min to synthesize poly(TBS) chains and then the required amount of DVB was added. Polymerization was terminated after 150 min.

All the polymer fractions were quenched with methanol and precipitated from methanol, filtered and dried under vacuum.

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) on-line detectors. Wyatt Technology ASTRA and EASI software and Waters BASELINE packages were employed for data collection and analysis. A series 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.

3. Results

TBS-DVB star microgels were prepared by the arm first method in two different solvents, a non-polar solvent heptane and a polar solvent THF using *t*-butyllithium as an initiator. The linear poly(TBS) arms were synthesized first, followed by the addition of different amounts of DVB in the appropriate solvent. The feed ratios and reaction conditions are summarized in Table 1.

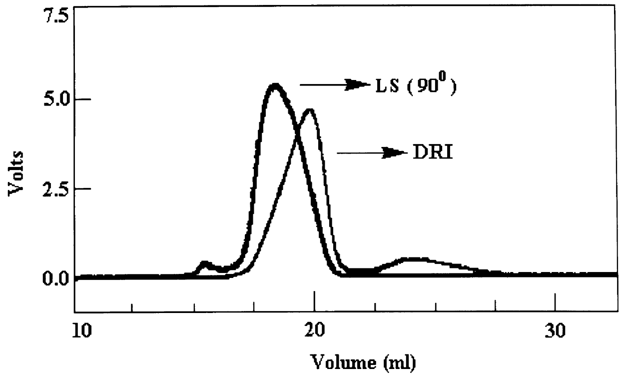

Fig. 2. SEC-DRI and SEC-MALLS traces of MDVBA (Heptane).

The samples of poly(TBS) chains were taken in each case before the addition of the crosslinking monomer and were analysed by SEC-DRI for molecular weight properties. The results are shown in Table 2. The molecular weight of the poly(TBS) chains is higher in heptane than in THF for the same ratio of *t*-butyllithium/TBS, but the polydispersity of the resulting polymer chains is much higher in heptane as evident from the SEC-DRI analysis (Table 2).

The star microgels were synthesized from the linear poly(TBS) chains by the addition of divinyl monomer DVB, which undergoes addition and crosslinking to form a central core. Table 2 shows the molecular weight properties of microgels formed in the two different solvents. The samples were analysed by SEC-DRI and SEC-MALLS. The DRI trace in Figs. 1 and 2 show some low molecular weight polymer in either solvent. The fraction of low molecular weight polymer is greater in heptane than in THF. This is due to slow initiation in heptane and is more like a tailing effect. This low molecular weight polymer at higher elution volume is not very obvious in the light scattering trace, as the intensity of the light scattering signal is proportional to the product of molecular weight and concentration. It is prominent in the DRI trace because the DRI detector responds to concentration of a particular species only. In Fig. 2, the small peak at low elution volume is due to very high molecular weight microgel particles, but the concentration of these particles is negligible as it is not visible in the concentration sensitive detector SEC-DRI trace.

The weight average molecular weight of the microgels is higher in the case of heptane and so is the polydispersity. The difference is the weight average molecular weight of microgels as determined by SEC-MALLS in the two solvents is higher when the amount of DVB used is about 30 mol%. This is close to the upper limit of divinyl monomers that can be used for microgel synthesis without any macrogelation. This difference decreased at lower levels of DVB as evident from the results in Table 2.

The formation of microgels in THF was also studied as a function of time (Table 3) after the addition of DVB. The molecular weight of microgels increases as a function of reaction time as found by our group previously in heptane [7]. However, the increase in the molecular weight of microgels in THF is not as great as in heptane.

Fig. 3 shows SEC-DRI traces for poly(TBS) arm and microgel samples MDVBA 151-156 taken at different times after the addition of DVB. Initially, the microgel sample exhibits two diffused peak maxima in the DRI trace, but with time the low molecular weight peak maxima at higher elution volume starts decreasing and after 60 min the microgel samples shows mainly one peak with a small shoulder. The molecular weight of the microgel samples shifts to higher values with reaction time as expected (Table 3).

Table 3
Effect of reaction time on the properties of microgels prepared in THF

Sample[a]	Reaction time (min.)[b]	SEC-DRI[c]			SEC-MALLS[c]			
		$M_n \times 10^{-5}$	$M_w \times 10^{-5}$ (g/mol)	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$ (g/mol)	PD[d]	d*n*/d*c*[e]	RMS[f] (nm)
PTBSA16	60	0.051	0.055			—		
MDVBA151	15	0.38	0.48	1.07	1.48	1.39	0.160	13.4
MDVBA152	30	0.43	0.56	1.10	1.65	1.49	0.159	9.4
MDVBA153	60	0.57	0.81	1.75	2.72	1.55	0.158	12.6
MDVBA154	120	0.71	1.07	1.90	4.01	2.10	0.163	13.9
MDVBA155	180	0.81	1.23	2.18	4.51	2.06	0.163	13.7
MDVBA156	240	0.93	1.53	3.15	6.30	2.00	0.162	18.2

[a] PTBSA denotes linear poly(TBS) arm and MDVBA denotes microgel samples.

[b] Reaction time for microgel samples is time after the addition of DVB. TBS:DVB molar feed ratio is 70.56:29.44.

[c] SEC-DRI (SEC) and SEC-MALLS (SEC with on-line MALLS detector) were used to determine number average molecular weight (M_n) and weight average molecular weight (M_w).

[d] PD is Polydispersity (M_w/M_n).

[e] d*n*/d*c* is refractive index increment.

[f] RMS is the root mean square radius of microgels at the peak maxima as determined from Debye plots.

Fig. 4 shows the increase in weight average molecular weight of the microgels with reaction time by SEC-DRI and SEC-MALLS (Table 3). The increase in molecular weights in the second case is more than the first. This is because the microgels have different architecture to the linear polystyrene standards used to calibrate the SEC-DRI system. In the SEC-DRI method, fractionation of different molecular sizes is based on hydrodynamic volume rather than molecular weights, thus molecules having the same hydrodynamic volume can have different molecular weights. Thus true molecular weights were determined by SEC-MALLS as this method is not dependent on standards and gives absolute molecular weights of polymer. The difference in the molecular weights by the two methods demonstrates the compact nature of the microgels.

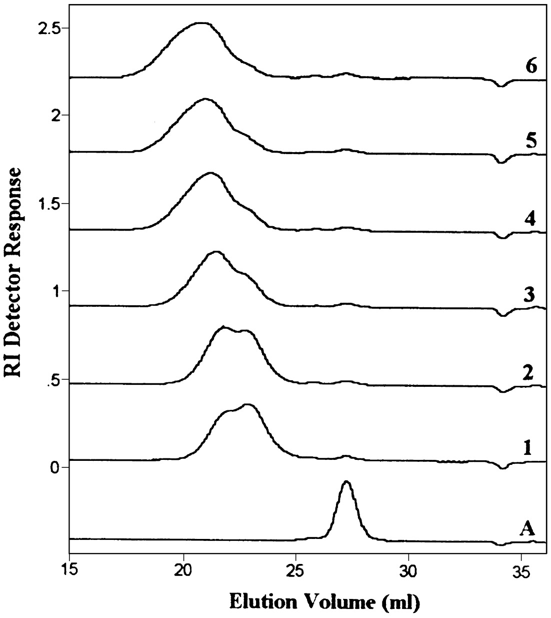

Fig. 3. SEC-DRI traces of MDVB151-156 (1–6) and PTBSA16 (A).

The refractive index increment d*n*/d*c* of the samples (Table 3) taken at different times is similar, which indicates no major change in the monomer composition in the microgel samples. The polydispersity of the microgels is very low in THF as compared to that of heptane [7]. Thus the polar solvent provides greater control over molecular weight distribution than the hydrocarbon solvent.

Differential molecular weight distribution of microgel samples taken at different times shows that the molecular weight of the microgels increased with time (Fig. 5) and the whole curve shifted to higher molecular weight indicating that all the polymer chains were active and participated in the formation of microgel particles.

Debye plots of various fractions of microgels (Table 3) show that the root mean square radius (RMS radius) sometimes called radius of gyration at the peak maxima decreased for MDVBA152 and MDVBA153 due to intramolecular crosslinking reactions and then started increasing slowly for the subsequent microgel samples. There is a sudden increase in the RMS radius for MDVBA156 sample. This may be due to the intermolecular linking reactions. The

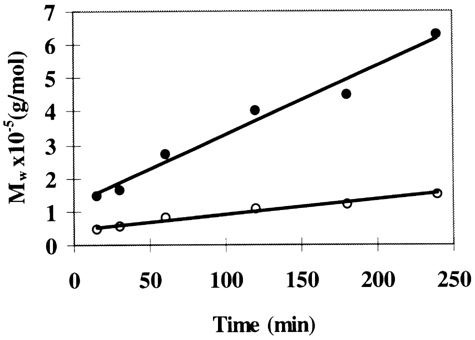

Fig. 4. Weight average molecular weight of microgels as a function of reaction time measured by SEC-DRI (○) and SEC-MALLS (●).

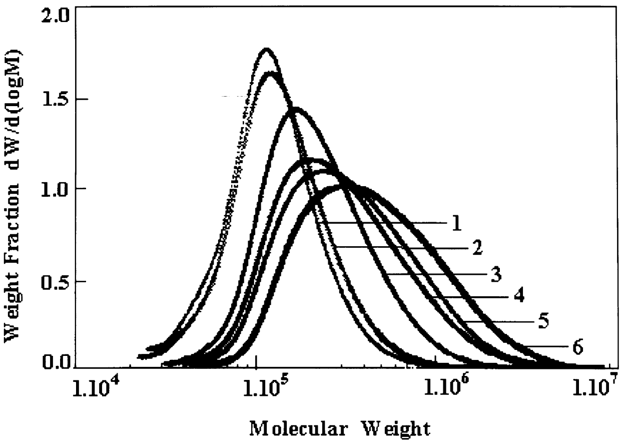

Fig. 5. Differential molecular weight distribution of microgels (MDVBA151-156) (1–6) (THF).

interparticle linking reactions occur much earlier in the hydrocarbon solvent than in the polar solvent and this is responsible for the higher molecular weight of the microgels in heptane than in THF. The particle size distribution was narrow initially and then started broadening with time (after 60 min) indicative of intra- and inter-crosslinking reactions. However, for the microgel sample (MDVBA156) at 240 min, the distribution was very narrow that probably indicates the end of the crosslinking reaction and the formation of microgel particles with narrow particles size distribution.

4. Discussion

Star microgels were synthesized using an anionic arm first method by a number of researchers. In this method, linear arms are formed first and then crosslinked using a small amount of divinyl monomers such as divinylbenzene. TBS-DVB microgels were synthesized in heptane using sec-butyllithium as an initiator by Okay et al. [5] and by our group [7]. We have used *t*-butyllithium as an anionic initiator in THF and heptane. The molecular weight distribution of poly(TBS) chains is effected by the performance of the initiator in a particular solvent, which is determined by the rate of initiation with respect to propagation. It is found that *t*-butyllithium initiates more slowly in hydrocarbon solvents such as heptane than in the polar solvent THF. *t*-Butyllithium exists in an associated much less reactive form in heptane and thus is consumed slowly over a period of time resulting in broad molecular weight distribution of the polymer. However, it is completely dissociated in the polar solvent THF, thus its reactivity is much higher and all the TBS chains are initiated over a relatively short period of time. This leads to a very narrow molecular weight distribution of poly(TBS) chains in THF as shown in Table 2. It has been shown by Morton et al. [12] that for styrene polymerization, the initiation is virtually complete before any noticeable polymerization in THF even at very low temperatures. The polymerization rate is effected by the association phenomenon and the temperature has considerable effect on the association equilibrium is non-polar solvent. Thus for a reasonable rate of polymerization, the reaction was carried out at 50°C in heptane. In contrast, the polymerization rate of TBS is fast even at −80°C in THF. The initiator has a pronounced effect on the polymerization of TBS in heptane. *t*-Butyllithium behaves as a good initiator in THF to synthesize linear poly(TBS) chains of narrow polydispersity.

The linear poly(TBS) chains with anionic ends were then used as an initiator for the polymerization of DVB to synthesize microgels. It has been proposed by Graham et al. [13] that in a thermodynamically good solvent the polymerizing chains act as steric stabilisers, thus preventing the close approach of microgel particles or their precursors. Heptane is a good solvent for poly(TBS) chains and poor solvent for poly(4-vinylstyrene) blocks. This explains why the linear block copolymer chains arrange themselves into micelles where the crosslinking reaction of the second double bond of DVB occurs in the case of heptane. Poly(TBS) chains stabilise the crosslinked core and prevent the precipitation of the polymer during the crosslinking reactions in heptane.

It was of interest to study the effect of a polar solvent such as THF that is a good solvent for both poly(TBS) chains and the poly(TBS)-co-(4-vinylstyrene) block copolymer formed during microgel synthesis. It is proposed that the mechanism of microgel formation is different in two solvents (Fig. 6). In heptane, the microgels are formed by intramolecular crosslinking reaction within the micelles. However, in THF, first linear co-polymer of poly(TBS-co-vinylstyrene) is formed until virtually the total amount of DVB in the reaction medium is consumed and then the linking reactions take place in solution leading to the formation of macromolecules. These macromolecules undergo intramolecular crosslinking reactions resulting in the formation of the microgels. The term intramolecular crosslinking has a different meaning in the case of the microgels as compared to the normal organic synthesis. Here, intra- means within the macromolecule or micelle rather than within the same molecule as in the case of organic synthesis. As a result of different mechanisms in the two solvents, heptane and THF, the final structure of the microgel particles will be different. Microgels with small and compact central core will be formed in heptane whereas the microgels synthesized in THF will have a larger and loosely crosslinked central core. The molecular weight and polydisperisty of microgels is effected in a similar manner as in the case of the polymerization of TBS in two different solvents, heptane and THF. Besides micelle formation in heptane, association of polymer chains in heptane has a marked effect on the molecular weight properties of microgels. The associated species and the micelle formation in heptane promote the intermolecular linking and intramolecular crosslinking reaction respectively, leading to the formation of microgels with

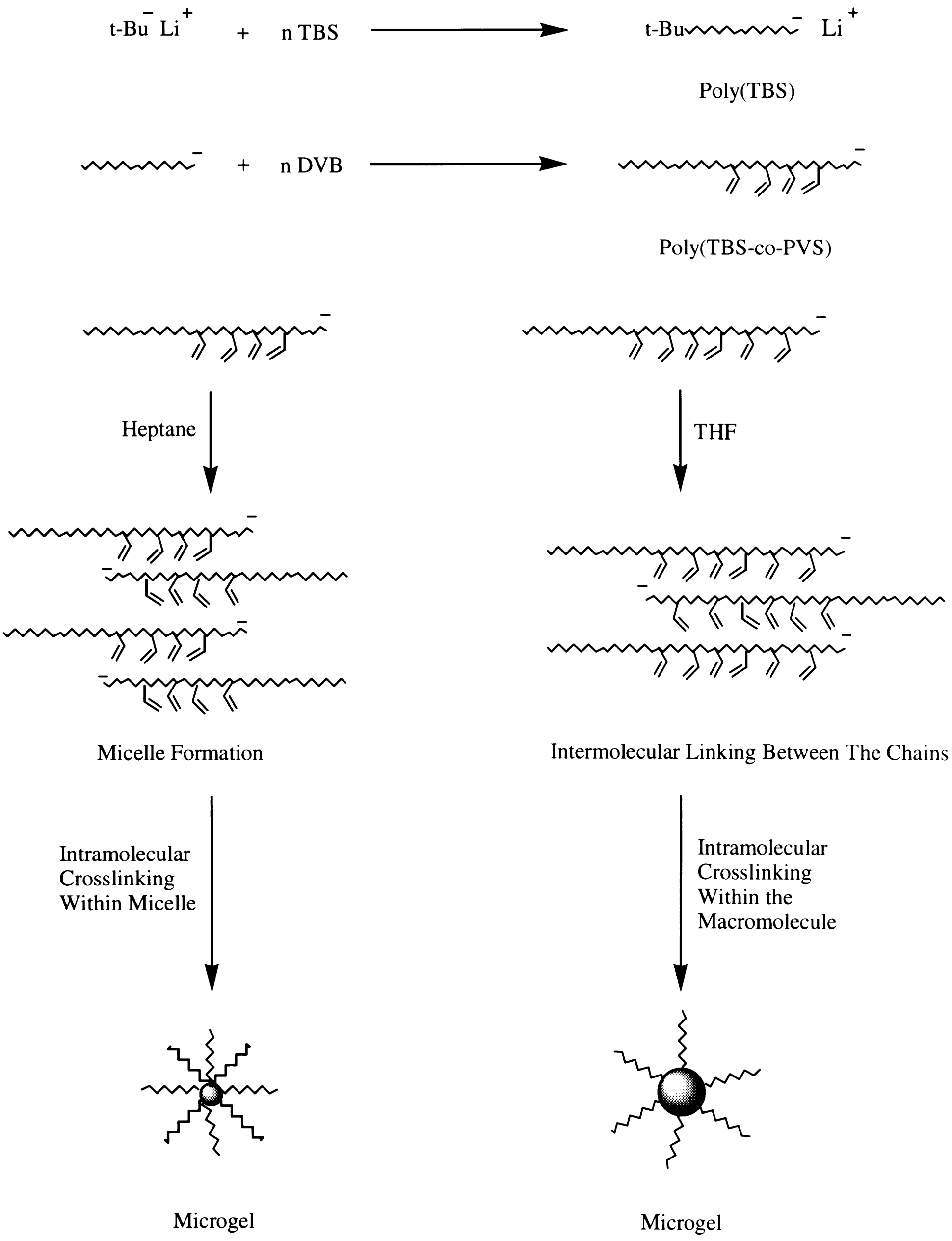

Fig. 6. Schematic representation of microgel formation in anionic polymerization.

highly crosslinked central core. While in the case of THF, the polymer chains are solvated by the solvent molecules and the nature of these species is different from the associated form. In solvating medium such as THF, the active centres are free carbanions with loose and tight ion pairs and due to repulsive attraction between these anions, the extent of intermolecular linking is less in THF and thus the number of arms per microgel molecule varies in two solvents. This also explains the lower molecular weight in THF. The difference in the molecular weight and polydispersity of microgels in the two solvents is attributed mainly to the nature of the solvent, which results in the formation of different species in a particular solvent and to some extent the behaviour of initiator in these two solvents. The initiator is responsible for the tailing effect in heptane.

The results of microgel formation as a function of time in THF using *t*-butyllithium are also compared with the results published by Pille et al. [7] with heptane as a solvent and sec-butyllithium as an initiator for similar TBS:DVB feed ratios. It is found that *t*-butyllithium in THF and sec-butyllithium in heptane are good initiators in the respective solvents and resulted in narrow molecular weight distribution of poly(TBS) chains. The molecular weight of microgels is higher in heptane, but the polydispersity of microgels is very narrow in the case of THF as compared to heptane for similar feed ratios. Similar values of d*n*/d*c* indicate similar composition of microgels in these two cases. Comparison of the results of this work (Table 3) with the earlier work of Pille et al. [7] shows only a small difference in the weight average molecular weight of microgels as determined by SEC-DRI at any reaction time. However, the SEC-MALLS weight average molecular weight of microgels is higher in heptane [7] as compare to THF. This indicates the formation of highly compact microgels in heptane.

A similar trend was found in the case of heptane when *t*-butyllithium is used as an initiator. Even though the initiator is different in these two cases, the results confirm that the microgels are formed by the same mechanism in heptane.

5. Conclusions

It is concluded that solvent plays an important role in the formation of microgels by anionic polymerization. In the case of TBS/DVB microgels, the polar solvent THF provides better control over molecular weight distribution of the resulting microgels than a non-polar solvent such as heptane. Association phenomenon of initiator in non-polar solvent results in slow initiation with respect to propagation of polymer chains leading to broad molecular weight distribution of poly(TBS) chains. This also contributes to a long tailing effect and intermolecular linking reactions in the resulting microgels. In the case of a polar solvent such as THF, the polymerization of the first double bond of DVB results in the formation of a linear block polymer. The crosslinking reaction occurs later after virtually all the first double bonds are consumed in the propagation step. Owing to the repulsive interactions of carbanionic species in THF, the extent of intermolecular linking reactions is minimum and intramolecular crosslinking plays a major role in the synthesis and thus leads to the formation of microgels with uniform composition and narrow polydispersity.

Acknowledgements

S. Abrol would like to gratefully acknowledge The University of Melbourne for support in the form of a Melbourne University Postgraduate Scholarship. We would like to thank Dr. Greg Qiao for helpful discussions.

References

[1] Funke W, Okay O, Joos-Muller B. Adv Polym Sci 1998;136:139.
[2] Worsfold DJ, Zilliox J-G, Rempp P. Canadian J Chem 1969;47:3379.
[3] Eschwey H, Burchard W. Polymer 1975;16:180.
[4] Frater DJ, Mays JW, Jackson C. J Polym Sci: Part B Polym Phys 1997;35:141.
[5] Okay O, Funke W. Macromolecules 1990;23:2623.
[6] Okay O, Funke W. Makromol Chem Rapid Commun 1990;11:583.
[7] Pille L, Solomon DH. Makromol Chem Phys 1994;195:2477.
[8] Tsitsilianis C, Lutz P, Graff S, Lamps J-P, Rempp P. Macromolecules 1991;24:5897.
[9] Tsitsilianis C, Voulgaris D. Makromol Chem Phys 1997;198:997.
[10] Tsitsilianis C, Lutz P, Graff S, Lamps J-P, Rempp P. Macromolecules 1991;24:5897.
[11] Wiley RM, Jin JI, Kamath Y. J Polym Sci 1968;A1(6):1065.
[12] Morton M, Fetters LJ, Bostick EE. J Polym Sci: Part C 1963;1:311.
[13] Graham NB, Mao J, Urquhart A. Die Angewandte Makromoleculare Chemie 1996;240:113.