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Living dispersion polymerization of styrene in the presence of polystyrene-block-poly(4-trimethylsilylstyrene)

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Summary

Living polystyrene microparticles with average particle diameters varying between 0.5 and 3.8 µm were obtained via sec.-butyl lithium-initated anionic polymerization of styrene in n-hexane diluent when polystyrene-block-poly(4-trimethylsilylstyrene) was added as dispersing agent. The influence of block copolymer molecular architecture and concentration as well as polymerization temperature, monomer concentration and THF addition on polystyrene particle size, molecular weight and molecular weight distribution were investigated. In comparison to anionic styrene polymerization in cyclohexane solution, the anionic styrene dispersion polymerization in n-hexane was markedly slower.

Introduction

Non-aqueous dispersion polymerization represents an attractive route to tailor-made colloids with controlled architectures and surface functionalities. Characteristic feature of dispersion polymerization is that initiator, monomer, and diluent are miscible, whereas the polymer precipitates as soon as critical molecular weight is reached. In the presence of polymeric dispersing agents, preferably block and graft copolymers containing at least one segment which is compatible with the diluent, it is possible to prevent uncontrolled flocculation. Besides diluent polarity and reaction parameters such as monomer concentration and polymerization temperature, the molecular architecture of the polymeric dispersing agent is the key to controlled formation of colloidal particles. Such particles are of interest as reinforcing nano- and microfillers, pigments, and rheology modifiers in a wide range of applications.

While extensive work has been published on free radical non-aqueous dispersion polymerization (1-6), much less is known about living dispersion polymerization affording unique living colloidal particles as reactive colloidal intermediates for polymer synthesis. In contrast to aqueous dispersions, in non-

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aqueous dispersions living polymerization methods can be applied to control both microstructures and morphologies. Using functional chain-terminating reagents, well-defined functional groups can be introduced on colloidal particle surfaces. Furthermore, other monomers can be polymerized onto such particles to form core/shell or more complex multiphase microparticles. The attractive potential of living anionic styrene dispersion polymerization was outlined by Schwab and Murray (7). The objective of our research was to examine polystyrene-block-poly(4-trimethylsilyl-styrene) as dispersing agent for styrene dispersion polymerization in n-hexane diluent. Special emphasis was placed on the influence of block copolymer molecular architecture and reaction parameters on polystyrene particle formation and molecular weight distribution.

Experimental

Materials: polymerizations were carried out under dry argon (99,9999 % purity) which was passed through 4Å molecular sieve columns. The diluent n-hexane was refluxed over sodium, distilled off, mixed with n-butyl lithium (10 ml n-butyl lithium/1 l n-hexane), and distilled again into a glass vial. Styrene was extracted with aqueous KOH, refluxed and dried over CaH_2 and again over NaH dispersion. Prior to use, styrene was added to a flask containing dibutyl magnesium, condensed in vacuum into a break seal glass vial. 4-Trimethylsilylstyrene was prepared from 4-chlorostyrene and trimethylchlorosilane in a Grignard reaction as described in literatur (8,9). It was purified by refluxing and distilling under reduced pressure over CaH_2, and by stirring and finally by distilling it off a dibutylmagnesium solution under high vacuum into a break seal vial. The dispersing agent polystyrene-block-poly(4-trimethylsilylstyrene) was prepared by sec.-butyl lithium-initiated anionic polymerization of styrene followed by 4-trimethylsilylstyrene in benzene. The corresponding block copolymers were obtained in 90 to 94 % yield. Their properties are listed in Table 1.

Dispersion polymerization was carried out in a six-necked round bottom flask equipped with magnetic stirrer and thermocouple. After adding 100 ml n-hexane diluent and few droplets of styrene, sec.-butyl lithium solution in n-hexane (Aldrich, 1.3 mol/l) was added carefully until the color of the styrylcarbanion indicates absence of impurities. Then styrene (20 wt-% with respect to n-hexane) containing the dispersant and the sec.-butyl lithium initiator as solution in n-hexane are added. Usually the styrene/sec.-butyl lithium molar ratio was selected to afford polystyrene of M_n = 30000 g/mol. The polymerization was performed at 30 or 69 °C (reflux) and quenched after 2 h by adding methanol. For GPC analysis a portion of the dispersion was separated, the n-hexane was stripped off, polystyrene dissolved in THF, precipitated in methanol, dried in a vacuum oven at 50 °C and used for size exclusion chromatography (GPC) analysis of molecular weight and molecular weight distribution

(20 mg/ml chloroform solutions, Waters GPC equipped with Styragel Mikrogelset 1.1 columns and UV/RI detector and calibrated with polystyrene). For particle size analysis, the dispersion was diluted to 0.01 wt-%, sprayed on a carbon-coated copper grid and analyzed by transmission electron microscopy (Zeiss CEM 902) at 80 kV to determine the average particle sizes of the polystyrene particles.

Results and Discussion

When sec.-butyl lithium initiator is injected into a solution of styrene in n-hexane, growth of polystyrene chains is initiated. Depending on styrene concentration and reaction temperature, at a certain critical molecular weight, which was found to be approximately M_n = 4600 g/mol in n-hexane at 69 °C (7), polystyrene precipitates and immediately flocculates as indicated by drastic viscosity build-up and loss of process control. In the presence of a dispersing agent, which is accumulated at the particle surfaces, steric stabilization of the polystyrene particles prevents flocculation and chain growth continues in the polystyrene particles. In contrast to free radical polymerization, in anionic polymerizations all chains propagate at the same time and have the same molecular weight. Polystyrene-block-poly(4-trimethylsilylstyrene), containing 50, 60 and 75 wt-% polystyrene, was prepared as a new class of polymeric dispersant by sec.-butyl lithium initiated block copolymer synthesis. The properties of the three high molecular weight dispersants are listed in Table 1.

Table 1. Polystyrene-block-poly(4-trimethylsilylstyrene)

Sample no.	Polystyrene Content calc. (wt-%)	Polystyrene Content found (^{1}H-NMR) (wt-%)	M_n(GPC) (g/mol)	M_w/M_n(GPC)
P7525	75	77.5	109000	1.08
P6040	60	59.0	110000	1.12
P5050	50	48.6	179000	1.20

The dispersion polymerization was performed in n-hexane containing 10 and 20 wt-% styrene at 30 and 69 °C in the presence of polystyrene-block-poly(4-trimethylsilylstyrene) varying between 1 and 10 wt-%. As apparent from Table 2, 1 wt-% dispersant (PS04, PS03 in Table 2) was not sufficient to achieve steric stabilization and prevent uncontrolled precipitation. Obviously, such small amounts are insufficient to cover all particle surfaces. Usually 5 to 10 wt-% dispersant P7525 was required to afford controlled particle growth yielding particles of 0.5 µm diameter at 69 °C. Over the entire dispersant composition range (PS05 vs. PS11, PS18 vs. PS25, PS12 vs. PS26 in Table 2), the particles obtained at 69 °C were much smaller than those produced at 30 °C. Moreover, particle size distribution, as expressed by the standard deviation σ_{n-1} of the average particles sizes measured by transmission electron microscopy, was much narrower. Preferably, dispersion polymerization was carried out in refluxing n-hexane at 5 wt-% dispersant concentration. Interestingly, all polystyrenes prepared by dispersion polymerization exhibited narrow polydispersities M_w/M_n of approximately 1.05. Also number average molecular weights were in good agreement with those calculated from styrene/sec.-butyl lithium molar ratios.

Table 2. Anionic styrene dispersion polymerization in n-hexane[a)]

Sample no.	dispersant		temp.	styrene	particle size	σ_{n-1}	M_n[d)]	M_w/M_n[d)]
	PS (wt-%)	conc. (wt-%)	(°C)	(wt-%)	(nm)	(nm)	(g/mol)	
PS04	-	-	69	20	prec.[b)]	-	n.d.	n.d.
PS03	75	1	"	"	prec.[b)]	-	n.d.	n.d.
PS05	"	5	"	"	0.6	0.2	49000	1.05
PS10	"	10	"	"	0.5	0.3	59400	1.07
PS11	"	5	30	"	0.5	0.1	28900	1.04
PS18	60	"	30	"	2.1	1.0	34000	1.03
PS25	"	"	69	"	0.5	0.2	n.d.	n.d.
PS12	50	"	30	"	3.8	1.1	43600	1.04
PS26	"	"	69	"	0.9	0.3	47800	1.05
PS25	60	"	69	"	0.5	0.2	n.d.	n.d.
PS27	"	"	"	10	1.3	0.4	48400	1.05
PS22[c)]	"	"	30	20	2.1	1.5	n.d.	n.d.

a) 2 h, sec.-butyl lithium with monomer/initiator ratio selected to obtain M_n = 30000 g/mol; b) uncontrolled precipitation; c) sample equivalent to PS18 but THF was added at THF/sec.-butyl lithium molar ratio of 4; d) measured by GPC, n.d.: not determined.

When the Lewis base THF was added during polymerization (PS22), polymerization rate increased markedly. However, in the presence and absence of THF (cf. PS22 versus PS18) identical particle sizes of 2.1 µm with similar particle size distributions were obtained. With decreasing monomer concentration (PS27 versus PS25), larger particles were formed. This results from changes of the diluent polarity which affects nucleation and particle growth.

Molecular architecture of the dispersant, especially the weight ratio of the polystyrene and poly(4-trimethylsilylstyrene) played an important role. As a rule, with decreasing content of polystyrene segment, which is immiscible with the n-hexane diluent, the average particle sizes increased from 0.6 to 0.9 µm at 69 °C (PS05, PS25, PS26) and much more pronounced at 30 °C from 0.5 to 3.8 µm. In view of dispersion stability, the dispersant containing 75 wt-% polystyrene segment was preferred over the other diblock copolymers containing more of the poly(4-trimethylsilylstyrene) segment. This experimental result is in accord with observation of Schwab and Murray (7) for the polystyrene-block-poly(4-tert.-butylstyrene) dispersant.

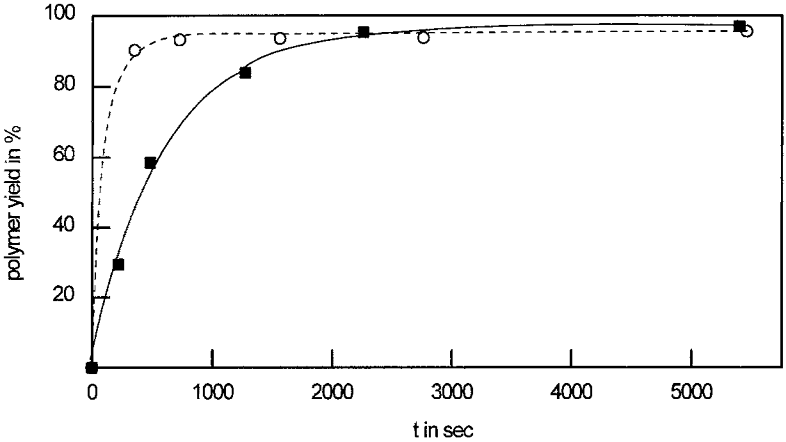

Fig. 1. Styrene solution polymerization in cyclohexane (O) compared with styrene dispersion polymerization in n-hexane (■) at 44 °C and styrene/sec.-butyl lithium molar ratio of 290.

As apparent from Fig.1, styrene dispersion polymerization in n-hexane diluent is markedly slower than styrene polymerization in cyclohexane solution using identical reaction conditions. Since both solvents have similar polarities, the slower polymerization rate of the dispersion polymerization must be related to monomer partitioning accounting for lower local styrene concentration at high conversions.

Conclusion

In conclusion, with increasing content of polystyrene segments in polystyrene-block-poly(4-trimethysilylstyrene) dispersants, increasing polymerization temperature and increasing concentrations of monomer and dispersing agent, the average particle sizes decreased. Polystyrene with average particle sizes ranging between 0.5 and 2.1 µm can be produced at 20 wt-% styrene concentration, whereas anionic microgeltype particle synthesis requires extremely low styrene concentrations. Narrow polystyrene polydispersities $M_w/M_n < 1.05$ indicate that the carbanions at the polystyrene are readily accessible for styrene monomer. Consequently also other reagents and other monomers are likely to react with the chain ends, thus producing a wide variety of colloidal polymer particles with controlled functionalities and particle architectures.

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