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Comparison of Controlled Radical Styrene Polymerizations in Bulk and Nonaqueous Dispersion

Matthias Hölderle, Martin Baumert, and Rolf Mülhaupt*

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs Universität, Stefan-Meier Strasse 21, D-79104 Freiburg i.Br., Germany

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Introduction. Nonaqueous dispersion polymerization[1−4] is a very versatile method to afford polymer dispersions of controlled morphology. It is initiated in a homogenous medium where all components are miscible. When polymer molar mass exceeds a critical limit, polymers phase separate and aggregate. Steric stabilization of polymer particles is achieved when dispersing agents, usually block copolymers, are added. After formation of particles, further polymerization occurs in bulk of the monomer-swollen particles. Provided that no new particle nucleation takes place, it is possible to obtain narrow particle size distributions. Particle sizes depend mainly upon the solubility of the formed polymer in the medium. In case of better solubility, aggregation of polymer chains is delayed, resulting in larger diameters of the formed particles. Low solubility causes quick aggregation and therefore smaller particle sizes.

Advanced methods like living anionic polymerization[5,6] and group transfer polymerization[7,8] (GTP) have been performed in nonaqueous dispersions although most research is concerned with free radical polymerization. Living dispersion polymerization gives both control of molar mass and particle morphology.

Controlled radical polymerization[9−12] is a new living polymerization technique using for example 2,2,6,6-tetramethyl-1-piperidyloxy radical (TEMPO) combined with azoisobutyronitrile or benzoyl peroxide (BPO) as initiating system.[13,14,15] Preferably controlled radical styrene polymerization is performed in bulk at temperatures of 100−140 °C. This leads to high viscosities and therefore experimental problems related to stirring at high conversions.

Combining controlled radical polymerization and nonaqueous dispersion polymerization should provide the above-mentioned advantages of a living polymerization method and lead to a low viscosity product even at high conversions. In this study living radical polymerization in bulk and nonaqueous dispersion are compared with respect to reaction kinetics and control of polystyrene molar mass. Moreover particle formation during controlled radical styrene dispersion polymerization is investigated.

Experimental Section. (a) Materials. Styrene obtained from Fluka was stirred over lithium aluminium hydride for one night and distilled under reduced pressure. TEMPO, BPO (Aldrich), and decane (Fluka) were used as received. The dispersant Kraton G1701, supplied by Shell Chemical Co., is a polystyrene-*block*-poly(ethene-*alt*-propene) with a polystyrene content of 34 wt %. The number average molar mass of the PS block is 35 700 g/mol and of the poly(ethene/-*alt*-propene) is 68 300 g/mol. Prior to use it was dissolved in THF, precipitated from methanol, and dried over night in a vacuum oven.

(b) Polymerizations. The dispersion polymerizations were carried out in a flask equipped with a magnetic stirrer bar under argon atmosphere. Decane, styrene, Kraton G1701, BPO, and TEMPO were mixed and degassed by two freeze−pump−thaw cycles using argon as inert gas. Then the flask was immersed into an oil bath at 135 °C for 70 h. Periodically samples were taken and analyzed. The samples were dissolved in THF, precipitated from methanol, and dried in a vacuum oven for 24 h.

The polymerizations in bulk were carried out in the same way without decane and dispersant. The polymerizations were stopped when the increasing viscosity prevented mixing by a magnetic stirrer (6.8−7.5 h).

(c) Particle and Polymer Characterization. For NMR measurements an AMR 300 spectrometer from Bruker with $CDCl_3$ as internal standard was used. The diameters of the polymer particles were determined by TEM using a Zeiss CEM 902 with 80 kV voltage. The samples were prepared by spraying diluted dispersions, containing approximately 0.01 wt % solids, onto carbon-coated copper grids. Image processing gave the number average of the particle diameter and the standard deviation.

Conversions were determined by ^{1}H-NMR, comparing integrals of olefinic and aliphatic protons (bulk polymerization). In case of dispersion polymerization the dispersant was used as a standard. The conversions were calculated from the ratio of aromatic to aliphatic protons, which increases with increasing conversion.

Molar mass was determined using a Waters size exclusion chromatograph calibrated against polystyrene and equipped with Microgelset a 11 columns (obtained from Polymer Lab, Mainz, Germany) and UV/RI detectors. In some cases molar masses of the polystyrene were similar to those of the dispersant. Here mathematical data processing was applied to separate the peaks.

Results and Discussion. Three polymerizations in bulk and dispersion were carried out by varying the TEMPO concentration from 0.012 to 0.042 mol of TEMPO/L of styrene using a TEMPO/BPO molar ratio of 1.6 and a reaction temperature of 135 °C. Polymerization results and polymer characterization are listed in Table 1.

As can be seen in Figure 1, bulk polymerization is much faster than dispersion polymerization. In bulk approximately 7 h and in dispersion 70 h are necessary to reach a plateau in the conversion/time plot, thus reflecting the lower overall monomer concentration in dispersion where decane dilutes styrene monomer. The conversion/time plot of the dispersion polymerization for the lowest, calculated molar mass of $M_n = 22\,000$ g/mol shown in Figure 1A (run D22) exhibits an unusual shape. The polymerization starts slowly and accelerates after 30 h simultaneously with the onset of turbidity resulting from particle formation. This is reasonable since the particles, once formed, are swollen with monomer leading to a higher local styrene concentration and consequently higher reaction rates. The sample collected before this onset of particle formation was transparent at the reaction temperature but became turbid at room temperature. This indicates that new particles are formed upon cooling, most likely in addition to particles formed during polymerization. In runs D50 and D75 turbidity occurs much earlier, which is

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* To whom correspondence should be addressed.

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Table 1. Polymerization Conditions and Characterization Data[a]

sample[b]	reaction time (h)	[TEMPO][c] (mol/l)	conversion (%)	M_n (g/mol) calcd[d]	M_n (g/mol) GPC	M_w/M_n (GPC)	diameter (nm)	σ (%)
D22	75	0.042	64	14 100	12 200	1.52	260	49
B22	5.8	0.013	69	15 200	15 500	1.19		
D50	69	0.018	71	35 500	42 500	1.29	1610	41
B50	7.5	0.005	78	39 000	37 300	1.15		
D75	69	0.012	65	48 800	51 400	1.41	1680	75
B75	7.4	0.004	81	60 800	53 400	1.27		

[a] Other reaction conditions: reaction temperature = 135 °C, [TEMPO]/[BPO] = 1.6, and content of dispersant = 10 wt % (samples D22, D50 and D75). [b] D or B means dispersion or bulk, respectively. Numbers 22, 50, and 75 denote the molar mass calculated for 100% conversion in 1000 g/mol. [c] In dispersion, a monomer concentration of 30 wt % in decane is used, thus lowering the overall TEMPO concentration by a factor of 0.3. [d] Molar mass calculated for the actually reached conversion.

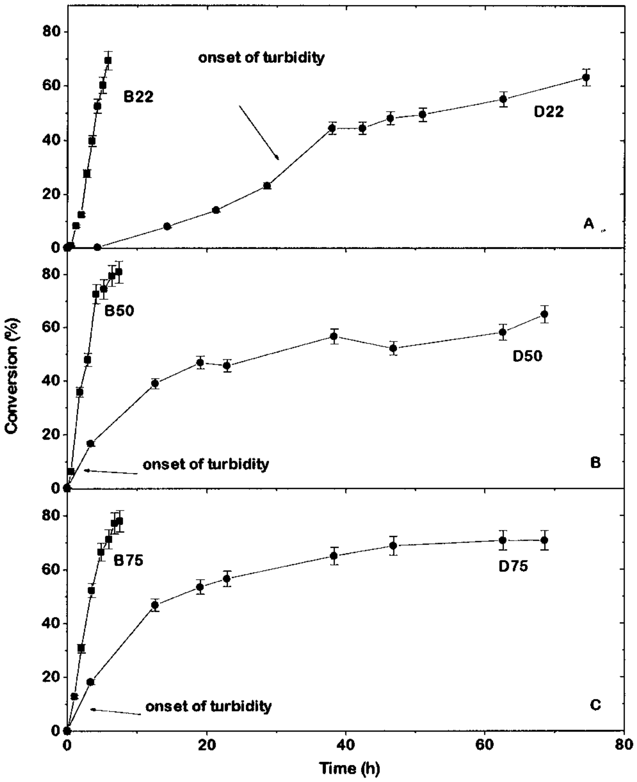

Figure 1. Conversion as a function of time for bulk and dispersion polymerization at different TEMPO concentrations.

attributed to the longer and therefore less soluble polystyrene chains. Early turbidity is associated with the absence of acceleration during the later stages of the polymerization.

Assuming a constant radical concentration and therefore first-order kinetics, plots of $\ln([M_0]/[M])$ vs time, where $[M_0]$ is the initial and $[M]$ is the monomer concentration at a certain time, should provide linear relationships. As can be seen in Figure 2 this is fulfilled only for bulk polymerizations. Most likely, in dispersion, a part of the polymer chains remains dissolved in the decane/styrene mixture and another part aggregates to form particles. Simultaneous polymerization in particle and solution could account for deviation from linear relationship between $\ln([M_0]/[M])$ and time. Different concentrations of TEMPO in decane and in the particles due to different solubilities affect the equilibrium of the reversible termination and therefore the radical concentration.

The molar masses depicted in Figure 3 are proportional to conversion, thus clearly demonstrating the living nature of this process. Bulk polymerization shows more pronounced linearity.

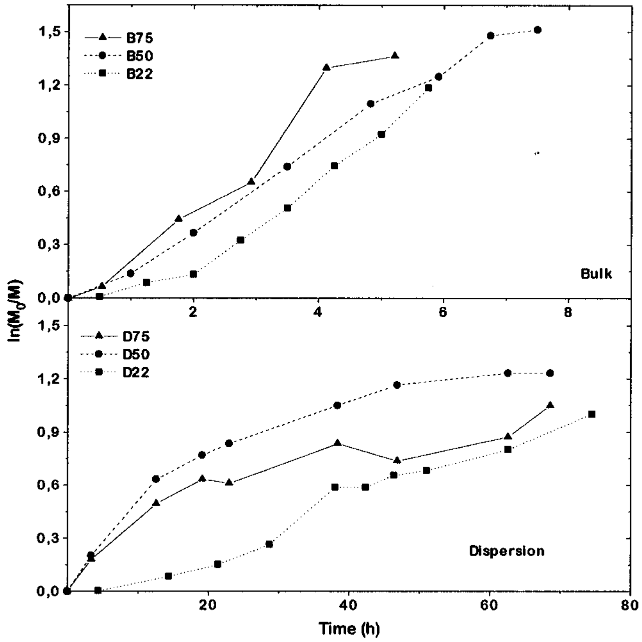

Figure 2. Polymerization kinetics of bulk and dispersion polymerization at different TEMPO concentrations.

As illustrated in Figure 3, especially at high molar mass of polystyrene, corresponding to very low TEMPO concentration, the molar masses found in dispersion polymerization are much higher than those of bulk styrene. This indicates that TEMPO is less effective in end capping free radicals when polymerizations are performed in dispersion. Moreover it should be taken into account that the reaction time of dispersion polymerization is much longer, resulting in a higher possibility of unwanted side reactions, e.g. recombination reactions. Polydispersities, listed in Table 1, are found to be much higher in dispersion polymerization compared to bulk polymerization. In Figure 4 the SEC traces for a typical dispersion polymerization are shown (run D22). Signal V is due to the dispersant, and signals I−IV show polystyrene at different conversions. It can be seen that the polydispersities increase with increasing conversion (from values of 1.2 up to 1.5 compared to 1.1−1.3 for bulk polymerization). This again reflects the presence of different active chain ends of polystyrene growing simultaneously in solution and in particles and the longer reaction time of dispersion polymerization when compared with bulk polymerization. The equilibrium of the reversible termination is affected by the TEMPO concentrations that vary in decane and in particles due to different solubilities of TEMPO.

Generally in nonaqueous dispersion polymerizations no new particles are formed, once particle nucleation

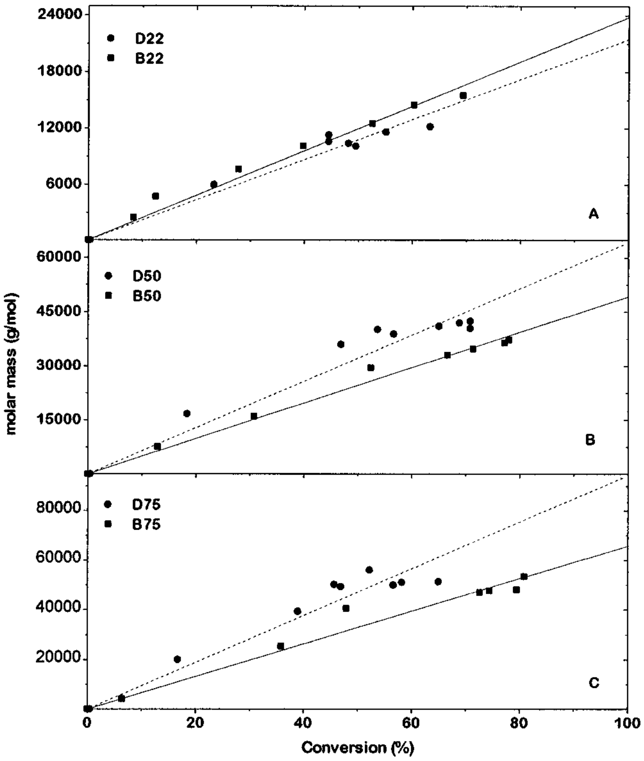

Figure 3. Correlation molar mass and conversion for bulk and dispersion polymerization at different TEMPO concentrations.

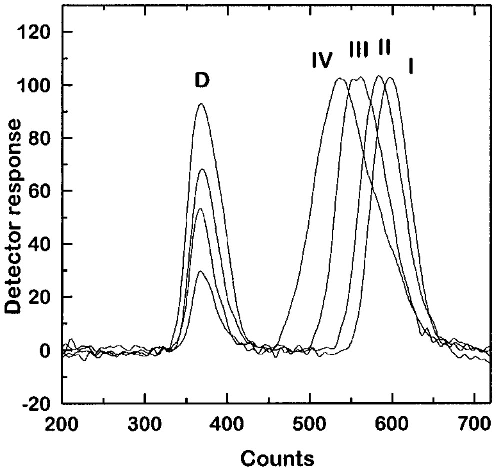

Figure 4. SEC traces of polystyrene samples taken at certain conversions (I, 14%; II, 23%; III, 45%; IV, 63%; dispersion polymerization run D22; signal D due to dispersant). The increase of M_n and the broadening of the distribution with conversion is shown.

has occurred. The growth of existing particles leads to narrow particle size distributions. In controlled radical dispersion polymerization, however, particle size distributions with diameters ranging from 50 nm to 10 μm (see Figure 5) were very broad. Therefore image processing by TEM can only provide a very rough estimation for the average particle diameters. The reason may be partial solubility of polystyrene chains, enhanced by high reaction temperature and styrene content and low molar masses, thus leading to particle formation on cooling.

Conclusion. Controlled radical polymerization in bulk as well as in nonaqueous dispersion affords polymers of controlled molar mass. Polydispersities in dispersion are higher than in bulk. In contrast to conventional dispersion polymerizations particle size distributions were very broad, which could be attributed to high reaction temperature. For better control of particle formation it is important to develop other initiator systems which initiate controlled radical dispersion polymerization at lower temperature.

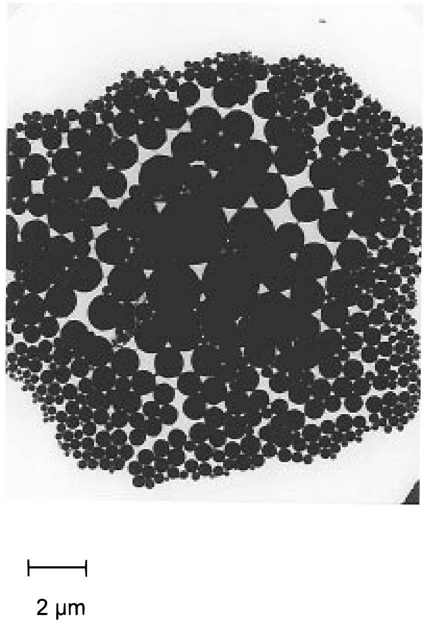

Figure 5. TEM micrograph of particles recovered after 12.6 h at 135 °C (run D75, Table 1).

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References and Notes

(1) Barett, K. E. J. *Dispersion Polymerization in Organic Media*; Wiley & Sons: London, 1975.
(2) Shen, S; Sudol, E.; El-Aasser, M. S. *J. Polym. Science Part A: Polym. Chem.* **1994**, *32*, 1087.
(3) Stejskal, J.; Kratochvil, P. *Makromol. Chem. Makromol. Symp.* **1992**, *58*, 221.
(4) Winnik, M. A.; Lukas, R.; Chen, W. F.; Furlong, P. *Makromol. Chem. Makromol. Symp.* **1987**, *10/11*, 483.
(5) Schwab, F. C.; Murray, J. G. Anionic Dispersion Polymerization of Styrene. In *Advances in Polymer Synthesis*; Plenum: New York 1985.
(6) Schneider, M; Mülhaupt, R. *Polym. Bull.* **1994**, *32*, 545.
(7) Jenkins, A. D.; Maxfield, D.; dos Santos, C. G.; Walton, D. R. M.; Stejskal, J.; Kratochvil, P. *Macromolecules* **1992**, *13*, 61.
(8) Hölderle, M.; Mülhaupt, R. *Acta Polym.* **1995**, *46*, 226.
(9) Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 133.
(10) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070.
(11) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.
(12) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.
(13) Georges, M. K.; Veregin, R. P. N.; Kazmaier; P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(14) Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993.
(15) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183.

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