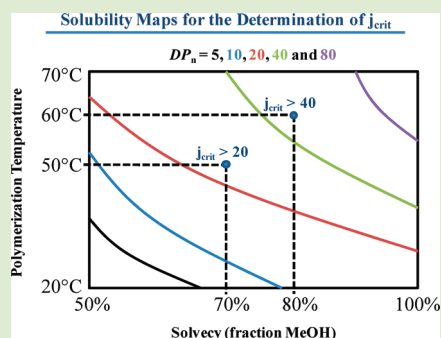


Determination of the Critical Chain Length of Oligomers in Dispersion Polymerization

Niels M. B. Smeets,[†] Robin A. Hutchinson, and Timothy F. L. McKenna^{*,‡}

Department of Chemical Engineering, Queen's University, 19 Division Street, Kingston, Ontario, Canada, K7L 3N6

ABSTRACT: The critical chain length (j_{crit}) in dispersion polymerization is systematically investigated utilizing low molecular weight poly(methyl methacrylate) oligomers synthesized by catalytic chain transfer polymerization. The solubility of these oligomers in methanol/water media of different compositions and at different temperatures has been visually determined. The results show that the solubility of the oligomers increases with increasing methanol fraction and increasing temperature. The constructed solubility map allows for an estimate of j_{crit} as a function of these important polymerization parameters. Furthermore, it is found that the value of j_{crit} changes with the concentration of the oligomers in the methanol/water medium, an important consideration for understanding the nucleation stage of a dispersion polymerization. The obtained results have been successfully correlated to earlier data reported on the dispersion polymerization of methyl methacrylate.



Dispersion polymerization is an attractive alternative to other dispersed phase polymerization processes, offering a facile route for the synthesis of micrometer-size monodisperse polymer particles from a single batch process. These polymer microspheres find widespread application as toners, column packing materials for chromatography, spacers for liquid crystal displays, and sensors for biomedical and biochemical analysis.^{1–3}

The unique characteristics of dispersion polymerization originate from the reaction medium, which is a good solvent for the monomer and polymeric stabilizer and a nonsolvent for the polymer formed. Consequently, a dispersion polymerization is a homogeneous solution prior to initiation. The polymer microspheres are formed according to mechanisms described by the aggregative and coagulative nucleation theories,⁴ which are originally derived from the homogeneous nucleation theory.⁵ The polymerization starts as a solution polymerization where radicals generated in the continuous phase propagate with monomer. The solubility of these oligomeric radicals is dependent on the chain length and the solvency of the medium. Propagation beyond a certain critical chain length (j_{crit}) causes these oligomers to precipitate and coagulate to form unstable precursor particles. Coagulation of these nuclei continues until sufficient stabilizer is adsorbed and steric stabilization is obtained. At this point, the polymer particles are colloidally stable and it is suggested that from here on no new nuclei or particles are formed. The existing polymer particles capture oligomeric radicals from the continuous phase and the polymerization proceeds as a pseudobulk polymerization to form micrometer-size monodisperse polymer colloids.⁶ However, this mechanism has not been conclusively established and it was recently reported that small nuclei are indeed formed continuously throughout the course of the polymerization.⁷

A crucial parameter in dispersion polymerization that governs the rate of the polymerization and the particle size distribution is the critical chain length, j_{crit} . Shen et al. summarized the influence of polymerization parameters on the particle size in the dispersion polymerization of MMA.⁸ The solvency (i.e., the composition of the reaction medium) and the polymerization temperature govern the solubility of oligomeric radicals in the reaction medium and, consequently, j_{crit} . The value of j_{crit} governs the rate of nuclei aggregation and the rate at which radicals enter the polymer particles, which both directly affect the particle size. However, to date, little attention has been paid to trying to identify values for this important parameter.^{9,10}

In a recent paper from our research group it was observed that in the presence of a cobalt(II)-based catalytic chain transfer agent the dispersion polymerization of MMA proceeded exclusively as a solution polymerization.⁷ No precipitation occurred during the polymerization and, consequently, no polymer colloids were formed. Cooling of the solution resulted in the precipitation of linear polymer chains with a number-average degree of polymerization (DP_n) of 28, suggesting that for this particular dispersion polymerization formulation at a polymerization temperature of 60 °C the j_{crit} value has to be larger than 28. It therefore appears that using these cobalt(II)-based catalytic chain transfer agents might be a useful method to investigate the solubility limits for dispersion polymerization.

In the current paper, we present a rapid approach to identify j_{crit} and demonstrate it by looking at the dispersion polymerization of methyl methacrylate (MMA). The solubility of poly(MMA) oligomers of different molecular weights in the

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Table 1. Analysis of the Poly(methyl methacrylate) Oligomers Used for the Determination of j_{crit}

	COBF [ppm]	DP _n (SEC) [-]	M _n [g·mol ⁻¹]	D [-]	DP _n (NMR) [-]	M _n [g·mol ⁻¹]
0.5k	13.0				4	420
1k	5.0	10	1159	1.66	8	814
2k	2.5	21	2454	1.75	17	1682
4k	1.0	42	4417	1.90	40	4022
8k	0.63	95	8748	2.18	93	9311

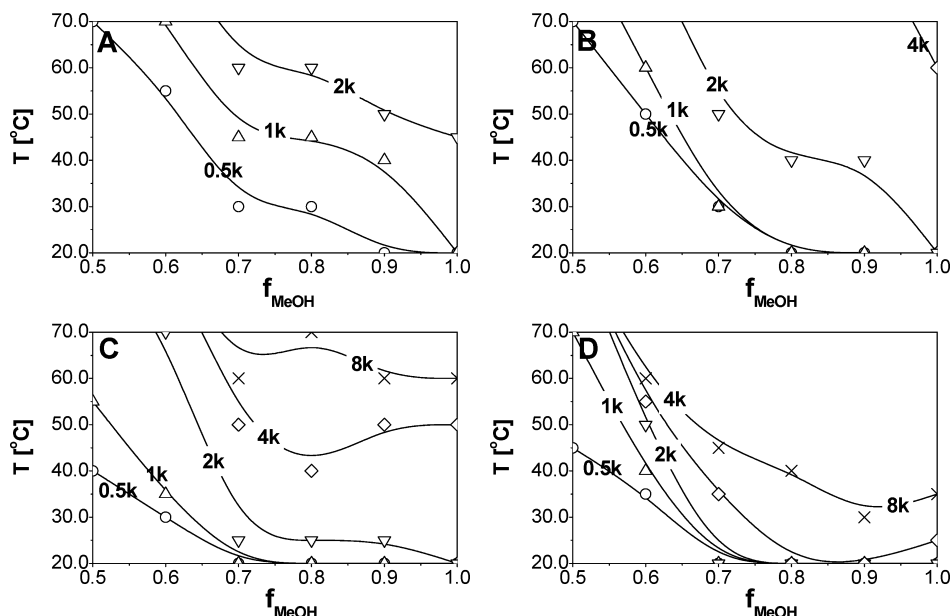


Figure 1. Solubility of poly(methyl methacrylate) oligomers of different molecular weights at different concentrations as a function of the temperature and the fraction of methanol in the solvent mixture: (○) 0.5k, (Δ) 1k, (▽) 2k, (◇) 4k, and (×) 8k; (A) poly(MMA) = 10⁻³ M, (B) poly(MMA) = 10⁻⁴ M, (C) poly(MMA) = 10⁻⁵ M, and (D) poly(MMA) = 10⁻⁶ M.

continuous phase of a dispersion polymerization is evaluated to provide an indication for the value of j_{crit} at different temperatures and different solvencies (i.e., different fractions of methanol) in the polymerization of methyl methacrylate (MMA). Although the concept of j_{crit} is similar in both emulsion and dispersion polymerization, here we will focus solely on dispersion polymerization. The nature of the continuous phase in a dispersion polymerization makes studying the value of j_{crit} more practical as the solubility limit of oligomers is increased due to the presence of methanol.

Poly(MMA) oligomers are synthesized using catalytic chain transfer polymerization (CCTP), which is an established controlled free-radical polymerization technique for the synthesis of polymers with a predetermined number-average degree of polymerization (DP_n) and a molecular weight distribution (MWD) with a dispersity (D) of approximately 2.^{11–17} The oligomers are synthesized in solution polymerization using [(difluoroboryl) dimethylglyoximate]cobalt(II) (COBF) and characterized by size exclusion chromatography (SEC) and ¹H NMR spectroscopy (Table 1). The chain lengths of the poly(MMA) oligomers were targeted at 5, 10, 20, 40, and 80, and it can be seen from Table 1 that the DP_n, as determined by SEC and ¹H NMR analysis, of the synthesized oligomers closely matches the desired values. The D of the oligomers in all cases is approximately 2, which indicates efficient CCTP conditions. In the remainder of the paper, the nomenclature of the p(MMA) oligomers is as follows: 0.5k (DP_n = 4), 1k (DP_n = 10), 2k (DP_n = 21), 4k (DP_n = 42), and 8k (DP_n = 95). Stock solutions of these poly(MMA) oligomers

in tetrahydrofuran (THF) are prepared and aliquots transferred into 20 mL scintillation vials. After evaporation, an exact amount of the poly(MMA) oligomers is suspended in methanol–water (MeOH–H₂O) mixtures at different concentrations (f_{MeOH} , w/w basis). For all experiments, the solvency is varied from $0.5 \leq f_{\text{MeOH}} \leq 1.0$ and the temperature is varied from $20 \text{ °C} \leq T \leq 70 \text{ °C}$ (the boiling point of the reaction medium at $f_{\text{MeOH}} = 1$ equals 67 °C). The solubility of the poly(MMA) oligomers is evaluated at four different concentrations, ranging from 10⁻⁶ M to 10⁻³ M. The values for f_{MeOH} , temperature, and the concentration of the poly(MMA) oligomers align with values typically found in dispersion polymerizations of MMA.^{7,8,18,19}

The solubility of the poly(MMA) oligomers as a function of the temperature and the MeOH (f_{MeOH}) fraction in the reaction medium are presented in Figure 1. The solid lines in Figure 1 indicate the solubility limit of the corresponding oligomer at a certain concentration: at f_{MeOH} or temperatures higher than the solid line, the oligomer is fully soluble in the MeOH–H₂O mixture. The solubility limit was obtained from a visual observation of the solubility of the poly(MMA) oligomers in the MeOH–H₂O mixture at a given temperature, with the lines shown in Figure 1 a spline-fit of the corresponding data points. It can be seen from Figure 1 that with increasing temperature and increasing f_{MeOH} , poly(MMA) oligomers of increasing DP_n are fully soluble. Furthermore, it can be seen that the solubility limit (i.e., the solid line) shifts to lower temperatures and lower f_{MeOH} as the concentration of the poly(MMA) oligomers is lowered. At the highest poly(MMA)

concentration of 10^{-3} M, the 4k and 8k oligomers were completely insoluble, independent of the temperature and the f_{MeOH} . At the lowest poly(MMA) concentration of 10^{-6} M, all the oligomers are fully soluble for $f_{\text{MeOH}} \geq 0.7$ and a temperature ≥ 45 °C. This clearly demonstrates that for the determination of j_{crit} not only the temperature and f_{MeOH} are important, but also the radical concentration in the continuous phase (which governs the concentration of propagating and terminated poly(MMA) oligomers).

The results in Figure 1 show that the value of j_{crit} increases with increasing f_{MeOH} and temperature. This correlation between j_{crit} and the f_{MeOH} and temperature is as expected and has been used by many authors to explain observed effects on the particle size and width of the particle size distribution. Furthermore, these results suggest that the value of j_{crit} can change throughout the course of a polymerization as the concentration of poly(MMA) oligomers in the continuous phase changes due to termination and chain transfer events.

The steady-state radical concentration ($[R]$) in a solution, free-radical polymerization can be estimated from eq 1,

$$[R] = \sqrt{\frac{k_d[I]}{k_t}} \quad (1)$$

where $[I]$ is the initiator concentration and k_d and k_t are the rate coefficients of initiator dissociation and termination, respectively. Assuming a k_t value of $10^7 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-120}$ and a k_d value of 10^{-5} s^{-1} (for vazo67 at 60 °C),²¹ the steady-state radical concentration equals approximately 10^{-7} M. Consequently, the initial poly(MMA) concentration in the continuous phase is likely very low. However, as a significant fraction of the propagating radicals can undergo chain transfer or, more likely, bimolecular termination, the poly(MMA) concentration will increase as the polymerization progresses.

It can be seen from Figure 1 that, for the conditions used by Cockburn et al. (i.e., $T = 60$ °C, $f_{\text{MeOH}} = 0.70$),⁷ the expected j_{crit} value in the initial stages of the polymerization is larger than 80. Due to the presence of COBF the DP_n of the propagating radicals is restricted and no precipitation occurs (i.e., no propagating radicals reach the required critical chain length for precipitation). Consequently, the poly(MMA) concentration in the continuous phase increases and the value of j_{crit} will decrease accordingly. The poly(MMA) concentration in the continuous phase after 6 h of polymerization in the presence of both 50 and 100 ppm COBF is estimated to equal 6×10^{-3} M. Consequently, in this stage of the polymerization, the j_{crit} has decreased from 80 to a value close to 20. For the polymerizations mediated with 50 and 100 ppm COBF, polymer with a M_n of 2330 ($\text{DP}_n = 23$) and 1750 ($\text{DP}_n = 17$) $\text{g} \cdot \text{mol}^{-1}$ have been reported, respectively.⁷ This observation is in good agreement with the predicted solubility limit of $j_{\text{crit}} = 20$ at 10^{-3} M in Figure 1. Because the DP_n of the polymer is below j_{crit} , no precipitation should occur and no polymer particles will be nucleated. Moreover, it was reported that the polymerization mediated with 50 ppm COBF was close to the solubility limit as the reaction mixture appeared somewhat translucent.⁷ This observation also is in good agreement with the results presented in Figure 1. The DP_n for this polymerization equals 23, which is very close to (or even slightly above) the j_{crit} value. Consequently, some precipitation could be expected to turn the reaction mixture slightly opaque. These results also suggest that, although the DP_n of the oligomers in the continuous phase is low, precipitation will

eventually occur as the increasing poly(MMA) concentration drives the j_{crit} value downward. Therefore, particle formation will occur if the radical flux is sustained over a sufficiently long period of time.

For a conventional dispersion polymerization (e.g., in the absence of a catalytic chain transfer agent), the increase in the poly(MMA) concentration in the continuous phase is less dramatic. For $f_{\text{MeOH}} = 0.70$ and $T = 60$ °C, the value of j_{crit} could drop from higher than 80 (at 10^{-6} M) to about 40 (at 10^{-5} M). It should be noted that, in this evaluation of j_{crit} , the influence of the monomer (MMA) on the solvency was not taken into account. This was deliberately done so to circumvent complications arising from the consumption of monomer during the polymerization and partitioning of the monomer between the continuous and dispersed phase.

The results presented here shed a more detailed light on the progression of j_{crit} in a typical dispersion polymerization system and contribute to furthering the understanding of the mechanism of particle formation in dispersion polymerization.

■ EXPERIMENTAL METHODS

Materials: The monomer, methyl methacrylate (MMA, Aldrich, 99%), was passed over a column of basic aluminum oxide (Aldrich, ~150 mesh 58A) to remove the inhibitor and stored at 5 °C prior to polymerization. The initiator, 2,2-azobis(2-methylbutanenitrile) (vazo67, Dupont) was recrystallized from methanol. Solvents, methanol (MeOH, Fischer Scientific), tetrahydrofuran (THF, Fisher Scientific), and toluene (Fisher Scientific), were used as received. For all experiments, distilled, deionized water was used, purified by a Millipore Synergy ion exchange unit. The catalytic chain transfer agent bis[(difluorononyl)dimethylglyoximate]cobalt(II) (COBF) was prepared according to a previously reported synthesis route.²² The intrinsic activity of the catalyst was determined in MMA bulk polymerization at 70 °C; $C_T = 20 \times 10^3$.

Synthesis of low molecular weight poly(methyl methacrylate): A COBF stock solution ($0.1 \text{ mg} \cdot \text{mL}^{-1}$) was prepared by dissolving COBF (1.5 mg, 3.6×10^{-3} mmol) in 15 mL of deoxygenated MMA. A typical polymerization (i.e., 2.5 ppm COBF) was performed as follows: Vazo67 (30 mg, 0.16 mmol) was dissolved in toluene (25 mL) and methyl methacrylate (22.5 mL, 0.21 mol) and purged with nitrogen for at least 1 h. Subsequently, an aliquot of the COBF stock solution (2.5 mL: 0.25 mg COBF, 6.0×10^{-4} mmol and 2.5 mL of MMA, 23 mmol) was added. The solution was then submerged in a preheated oil bath at 80 °C and the polymerization was continued for 5 h. The solution was cooled to room temperature and passed over a column of basic aluminum oxide to remove the cobalt(II) catalyst. Subsequently the polymer was precipitated in cold MeOH and dried under vacuum. The polymer was analyzed by size exclusion chromatography and ¹H NMR spectroscopy.

Solubility of low molecular weight poly(methyl methacrylate) in MeOH/water: The solubility of the different low molecular weight poly(methacrylate)s was determined at different concentrations (10^{-3} – 10^{-6} M), different temperatures (20–70 °C) and different MeOH/water ratios (50/50 to 100/0). Stock solutions of the different poly(methyl methacrylate)s were prepared in THF. Aliquots of these solutions were added to 20 mL scintillation vials and the THF was evaporated. Subsequently, 10 mL of the desired MeOH/water mixture was added. This suspension was stirred overnight. The solubility experiments were performed in a thermo-stated water bath. The solutions were introduced at a temperature of 20 °C and the solubility evaluated by visual inspection. Subsequently, the temperature was raised 10 °C and the solutions left at the new temperature for at least 30 min, prior to re-evaluation.

Analysis: ¹H NMR spectroscopy was performed on a 400 MHz Bruker instrument in deuterated chloroform. The number-average degree of polymerization (DP_n) was determined from the ratio of the integrals of the peaks of the vinyl protons at 5.3 and 6.0 ppm and the methoxy

protons at 3.2–3.8 ppm. Linear size exclusion chromatography (LSEC) was performed using a Waters 2690 separation module and a model 410 differential refractometer. A set of five Waters Styragel HR columns (HR5.0, HR4.0, HR3.0; HR1.0; HR0.5) were used in series at 40 °C. Distilled tetrahydrofuran (THF; Aldrich, 99%) was used as the eluent at a flow rate of 1 mL·min⁻¹, and the system was calibrated using narrow molecular weight poly(styrene) standards ranging from 374 to 400 × 10³ g·mol⁻¹. Mark–Houwink–Kuhn–Sakurada parameters used for the poly(styrene) standards:²³ $K = 1.14 \times 10^{-4} \text{ dL}\cdot\text{g}^{-1}$, $a = 0.716$ and for the poly(methyl methacrylate):²⁴ $K = 0.944 \times 10^{-4} \text{ dL}\cdot\text{g}^{-1}$, $a = 0.719$.

AUTHOR INFORMATION

Corresponding Author

*E-mail: timothy.mckenna@lcppp.cpe.fr.

Present Addresses

[†]Department of Chemical Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada, L8S 4L7.

[‡]C2P2-CNRS, UMR 5265, 43 Blvd du 11 Novembre 1918, Bât H. Curien – ESCPE, BP 2077, 69616 Villeurbanne Cedex, France.

Notes

The authors declare no competing financial interest.

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