SUPPORTING INFORMATION

Polymerization Induced Self-Assembly: Tuning of Nano-Object Morphology by Use of CO₂

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Experimental Section

Materials

2-cyano-2-propyl benzodithioate (CPBDT, 99% Aldrich), 1,1'-azobis(1-cyclohexanecarbonitrile) (V-40, 98%, Aldrich) Isopropanol (AJAX Finechem, AR grade) and liquid CO₂ (Coregas, 99.5%) were used as received. Styrene (>99%, Aldrich) was filtered through basic alumina to remove the inhibitor. 4-Vinylpryidine (4VP, >98%, Aldrich) was vacuum distilled before use.

Synthesis of CPBDT-terminated Poly(4-vinylpryidine) P4VP-CPBDT macro-RAFT agent

P4VP-CPBDT was prepared as follows: 4VP (4.0 g, 38.04 mmol), CPBDT (73.22 mg, 0.33 mmol), V-40 (6.736 mg, 0.027 mmol), and isopropanol (0.5 g) were added into a 20 ml glass bottle capped with a rubber septum and sealed with parafilm and copper wire. The bottle was purged with nitrogen for 30 min in an ice-water bath to remove air and sealed with vacuum grease. Polymerization was implemented in an oil bath under magnetic stirring at 90°C. Polymerization was stopped at prescribed times by cooling with ice water. The polymer was then recovered by precipitation in excess petroleum ether while stirring. The resulting product was dried in a vacuum oven at room temperature overnight. The molecular weight of dried P4VP-CPBDT was determined by gel permeation chromatography (GPC).

RAFT Dispersion Polymerization of Styrene in Isopropanol (without CO₂)

P4VP-CPBDT (57.6 mg, 0.0096 mmol), St (5.0 g, 48 mmol), V-40 (0.235 mg, 0.0009 mmol; using stock solution in isopropanol), and isopropanol (5.0 g) were successively added into a 3 ml glass vial with a magnetic stirring bar capped with a rubber septum and sealed with parafilm and copper wire. The vial was purged with nitrogen for 30 min in an ice-water bath to remove air and sealed with vacuum grease. Polymerization was implemented in an oil bath under magnetic stirring at 90 °C. Polymerization was stopped at prescribed times by cooling with ice water.

RAFT Dispersion Polymerization of Styrene in Isopropanol with CO2

Polymerization under CO₂ pressure was conducted in a custom-made sight gauge reactor with an internal volume of 40 mL. A detail description of the reactor setup is given elsewhere.¹ The reactor was cooled to 10 °C prior to the addition of any chemicals. P4VP-CPBDT (57.6 mg, 0.0096 mmol), St (5.0 g, 48 mmol), V-40 (0.235 mg, 0.0009 mmol), and isopropanol (5.0 g) were successively added into a 20 ml glass bottle with a magnetic stirring bar. After brief vortex mixing, the solution was transferred into the reactor. The solution in the reactor was purged with a constant flow of nitrogen for 30 min to remove oxygen. The system was heated to 90 °C with stirring. After equilibrium had been established, CO₂ was added into the reactor until the desired pressure was reached. Polymerization was stopped at prescribed times by first cooling the reactor to 10 °C over approximately 10 min, followed by depressurization. Monomer conversion was measured by gravimetry after drying of the resulting sample.

RAFT Dispersion Polymerization of Styrene in ethanol/water

Polymerizations were conducted with and without CO2 following the procedure mentioned above. Ethanol/water in a weight ratio of 80:20 was used as solvent to replace isopropanol during the preparation step.

Measurements and Characterization

Conversions of 4VP (synthesis of P4VP-CPBDT) were obtained by ¹H NMR (Bruker DPX 300 spectrometer at 300 MHz for hydrogen nuclei) in deuterated chloroform. Conversions of styrene (dispersion polymerizations) were obtained by gravimetry. A sample after polymerization was transferred to an aluminum dish and covered with perforated aluminum foil, and subsequently dried to constant weight in a vacuum oven at 40 °C.

Molecular weights (MWs) and molecular weight distributions (MWDs) were determined by gel permeation chromatography (GPC) with a Shimadzu modular system with dimethylacetamide (that contained 0.03% w/v LiBr and 0.05% w/v 2,6-dibutyl-4-methylphenol (BHT)) as eluent at 50 °C at a flow rate of 1.0 mL/min with injection volume of 100 μ L. The GPC was equipped with a DGU-12A solvent degasser, a LC-10AT pump, a CTO-10A column oven and an RID-10A refractive index detector, and a Polymer Laboratories 5.0 μ m bead-size guard column (50×7.5 mm) followed by four linear Styragel columns. The system was calibrated against polystyrene standards ranging from 500 to 10⁵ g/mol.

The sizes and morphologies of the block copolymer aggregates were observed using a transmission electron microscopy JEOL1400 TEM at an accelerating voltage of 100 kV. The solution of the block polymer in dispersion medium was directly taken and diluted with isopropanol. One drop of diluted sample was deposited onto copper grid (ProSciTech). 2% Phosphotungstic acid solution as negative staining was applied for all samples.

Offline DLS measurements were performed using a Malvern Zetasizer Nano Series running DTS software and using a 4 mW He–Ne laser operating at a wavelength of 633 nm and an avalanche photodiode (APD) detector. The scattered light was detected at an angle of 173°.

DLS scattering intensity measurements were performed in situ using a specifically designed Cordouan Particle Size Analyzer, with a 75 mW laser source operating at 658 nm in backscattering light detection mode. The backscattered light is recorded at 135° by an APD detector. The data were analyzed using NanoQ software. An issue that must be addressed here is whether expansion of the continuous phase (isopropanol/styrene) and to some extent possibly also the aggregates (that will be swollen with styrene to some extent) influence the DLS scattering intensity measurement. In other words, is the significant reduction in scattering intensity observed in the presence of CO_2 in Fig. 4 only caused by different morphologies between the two systems (with and without CO₂)? To test this, scattering intensity measurements were conducted on a polymerized system at 90 °C with and without CO₂. A raw latex prepared via PISA at 8.0 MPa CO₂ as detailed in the main text (the sample corresponding to the TEM image at the highest DP in Fig. 3, *i.e.* rod morphology) was loaded into the reactor. The scattering intensity was subsequently measured at 90 °C in the absence of CO₂, resulting in a value of 260 kHz (translucent appearance). The system was then pressurized with CO₂ to 8.0 MPa (at 90 °C) and the scattering intensity was once again measured, giving ~1400 kHz (turbid appearance). This increase in scattering intensity on pressurization can in principle be explained by: (i) A change in refractive index of the continuous and/or the dispersed phase, and/or (ii) a change in morphology from rods to entities that scatter more than rods. Now, given that it has been established (see main text) that the morphology obtained under CO₂ conditions does not revert back to the corresponding non-CO₂ morphology on depressurization, and the fact that PISA in the presence of CO₂ leads to smaller aggregates than without CO₂ (presence of CO₂ delays morphology development spheres-rods-vesicles), it appears unlikely that the increase in scattering intensity in these non-polymerizing systems is caused by a morphology change. However, it cannot be stated with certainty that the effect of CO₂ on a polymerizing system is the same as that on a nonpolymerizing system. It is thus clear that the much lower scattering intensity observed in the in situ measurements in Fig. 4 with CO₂ than without CO₂ is indeed caused by different morphologies of the two systems, as argued in the main text. An additional issue is the initial volume expansion associated with CO₂ pressurization, which is approximately a factor of 1.33, which would translate to a reduction in aggregate concentration by ~25%. This would, taken at face value, lead to a reduction in scattering intensity. However, this effect is small relative to the actual differences observed with/without CO₂ in Fig. 4. Expansion with CO₂ would also influence the viscosity of the continuous phase (isopropanol/styrene). However, in this case, only the scattering intensity is recorded (no analysis of the autocorrelation function), which is not affected by the viscosity. Thus, to conclude, we believe that the effect of CO₂ on the scattering intensity in Fig. 4 is mainly caused by a morphology change, although additional contributing factors cannot be excluded at this point.

The evolution of morphology during the polymerization illustrated in Fig. 5 was constructed based on TEM images as well as the online scattering intensity data in Fig. 4. The scattering intensity for the case with CO_2 displays three clear regions; (*i*) a flat region corresponding to spheres, (*ii*) a region of increasing scattering intensity corresponding to sphere and rods, and (*iii*) a region of again relatively constant scattering intensity corresponding to rods. The transition points between these regions (in terms of scattering intensity values) were used as guidance to construct also the phase diagram for the non-CO₂ case (using also TEM images).



Figure S1. Evolution of molecular weights and polydispersity index (PDI) as functions of monomer conversion for the synthesis of P4VP-CPBDT Macro-RAFT agent



Figure S2. Evolution of molecular weights distribution over reaction time for the synthesis of P4VP-*b*-PS in RAFT dispersion polymerization in isopropanol without CO_2 and CO_2 pressure of 8.0 MPa



Figure S3. Evolution of DP_n of P4VP-*b*-PS over polymerization time for RAFT dispersion polymerization of styrene in isopropanol without CO_2 and CO_2 pressure of 8.0 MPa



Figure S4. Evolution of monomer conversion over polymerization time for RAFT dispersion polymerization of styrene in isopropanol without CO₂ and CO₂ pressure of 8.0 MPa



Figure S5. Evolution of scattering intensity over reaction time measured *in situ* for RAFT dispersion polymerization of styrene in isopropanol without CO₂ and CO₂ pressure of 8.0 MPa

References

1. Pu, D.; Lucien, F. P.; Zetterlund, P. B. J. Polym. Sci.; Part A: Polym. Chem. 2011, 49, 4307-4311.