

Supplementary Material

Using Soluble Linear Polymers in Latent Biphasic Systems

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Experimental Section

All reagents and solvents were obtained from commercial sources without further purification unless otherwise specified. ^1H NMR spectrum were recorded on Varian VXR-300 or Unity p300 spectrometers at 300 MHz. Chemical shifts are reported in ppm with chloroform (7.27ppm) as an internal standard.

Tests of Polymer Separability/Recovery in the Toluene-Ethanol-Water

System. A sample of poly(*N*-octadecylacrylamide) containing 1 % of p-methyl red as a dye label (methyl-red labeled PNODAM) was prepared according to a reported procedure and dissolved in a mixture of 10 mL toluene and 10 mL 86% EtOH. Addition of 0.5 mL water (2.5% of the total volume) to the solution resulted in layer separation with the dye-labeled polymer visually residing in the upper toluene layer. Analysis by UV-visible spectroscopy showed the polymer had >1500:1 preference for the toluene layer.

Tests of Polymer Separability/Recovery in the Heptane-Ethanol-Water

System. A sample of poly(*N*-octadecylacrylamide) was dissolved in 20 mL of a solution containing equal portions of heptane and 96% ethanol. Addition of 9-10 drops of water

produced biphasic mixture. As in the toluene-aqueous ethanol system above, this dye-labeled PNODAM polymer was exclusively soluble in the heptane layer. UV-visible spectroscopy showed that the phase selective solubility was > 1500:1.

***N*-Octadecylacrylamide.** 26.7 g of octadecylamine was suspended in 500 mL of dichloromethane. 16.9 mL of triethylamine was added, and the mixture was cooled to 0°C using an ice-water bath. 8.9 mL of acryloyl chloride was dissolved in 50 mL of dichloromethane, and added dropwise to the amine suspension. The mixture was stirred at room temperature for 1 h. Dichloromethane was removed under reduced pressure and the residue was taken up in 250 mL of chloroform, washed with water and brine, dried over sodium sulfate and filtered. The filtrate was rotavapped and taken up in 100 mL of acetone with warming. 80 mL acetone was added and the mixture was allowed to sit at room temperature in dark to crystallize. ¹H NMR: δ6.3(d, 1H), δ6.1(dd, 1H), δ5.6(d, 1H), δ3.3(q, 2H), δ1.5(t, 2H), δ1.3(bs, 30H), δ0.9(t, 3H).

Poly(*N*-octadecylacrylamide-co-NA SI)(PNODAM-NA SI). The *N*-octadecylacrylamide monomer (12.94 g) and 676 mg of *N*-acryloxysuccinimide were dissolved in tBuOH at 70°C under nitrogen. Then AIBN (40 mg) in tBuOH was added at this temperature. The resulting polymerization mixture was stirred at 70°C for 16 h and then cooled to room temperature. The solvent was removed at reduced pressure using a rotary evaporator. The crude product copolymer was purified by repeatedly dissolving in CH₂Cl₂ and precipitating into 700 mL of methanol yielding ?? g of product: ¹H NMR: δ3.3(q, 14H), δ2.9(bs, 4H), δ1.8-1.3(br, 38H), δ1.2(bs, 210H), δ0.8(t, 21H).

Dye-labeled PNODAM-supported DAAP catalyst. A sample of the 4:1 PNODAM-PNA SI copolymer (4 g) prepared as described above was dissolved in

chloroform and first allowed to react with 50 mg of amine-terminated methyl red¹ at room temperature overnight. Then 500mg of the amine-terminated DAAP catalyst² in chloroform was added. After overnight stirring, a final portion of 1g of *N*-octadecylamine was added to quench any remaining active esters. After overnight stirring ?? g of the red polymer product was isolated by methanol precipitation. The polymer was characterized by UV-visible spectroscopy ($\lambda_{\text{max}} = 419$ nm in heptane). Based on GPC analysis (DMF, 0.01 M LiBr, TOSOH BIOSEP column) of an analogously prepared PNIPAM polymer, the molecular weight (M_n) of this product and the PDI were 800,000 Da and 1.9, respectively.

Acylation using PNODAM-Supported DAAP Catalyst. An equimolar mixture of 1 mmol of the substituted phenol and di-*tert*-butyl dicarbonyl was dissolved in 10 mL of ethanol. Then a heptane solution containing 97 mg of the PNODAM-supported DAAP catalyst (1 mol%) was added and the mixture was stirred for 30 min. Phase separation was achieved by the addition of 1.5 mL of water and the aqueous ethanol phase was concentrated and extracted with dichloromethane to obtain the product. The heptane phase was recovered and mixed with fresh substrate solution in ethanol for the next catalytic cycle.

Poly(maleic anhydride-*c*-octadecyl vinyl ether) (PMAOVE). Maleic anhydride was recrystallized from benzene before use. In a typical copolymerization, maleic anhydride (3.3 g, 33.7 mmol) and octadecyl vinyl ether (10 g, 33.7 mmol) were dissolved in 30 mL of benzene. The reaction flask was then evacuated and backfilled with nitrogen five times. After heating the resulting solution to 60 °C, 2 mL of a toluene solution of benzoyl peroxide (10 mg, 0.041 mmol) was added to initiate the

polymerization. After 20 h at 60 °C, the reaction mixture was diluted with 40 mL of ether and poured into 900 mL of acetone to provide of a white powder. This precipitate was filtered and dried to yield 10.5 g (79%) of the desired product polymer: ^1H NMR (CDCl_3 , δ): 0.83 (t, 3 H), 1.1-1.6 (br m, 36H), 2.8-3.7 (br s, 4.5H), 3.8-4.5 (br s, 1.5 H); IR (KBr, cm^{-1}): 1859, 1781, 1724, 1465. GPC (solvent, column) analysis of a N-benzyl imide derivative of this product showed it had $M_n = 730,000$ and $M_w = 1,950,000$

PMAOVE Substituted with Octadecylamine and Morpholine. PMAOVE (1 g, 2.5 mmol) was dissolved in 50 mL of CH_2Cl_2 and allowed to react with a mixture of octadecylamine (1.36g, 5.0 mmol) and morpholine (442 mg, 5.0 mmol) in 25 mL of CH_2Cl_2 . The reaction was stirred overnight. Acidic ion-exchange resin, Amberlyst-15 (4 g) was added to the reaction and the mixture was shaken overnight to remove any unreacted amines. The resin was filtered and washed with CHCl_3 . The filtrate was freed of solvent under reduced pressure to yield the product amic acid-containing polymer as a solid (IR stretches at 1716, 1641, 1575, and 1467 cm^{-1}). This polymer was then dissolved in 250 mL of toluene and heated at reflux overnight using a Dean-Stark trap to remove water. The product solution was then concentrated under reduced pressure to yield a solid that was dissolved in 100 mL of CH_2Cl_2 . The solvent was removed under reduced pressure using a rotory evaporator to give 1.1 g (65 %) of a light yellow solid: ^1H NMR (CDCl_3 , δ): 0.83 (t, 3H), 1.1-1.4 (br s, 27H), 1.4-1.6 (br s, 2H), 2.8 (br s, 1H), 3.3-3.5 (br s, 2.2H). IR (KBr, cm^{-1}): 1772, 1700, 1465, 1382. The presence of $-\text{CO}_2\text{H}$ groups was verified by IR spectroscopy after treatment with Et_3N : 1772, 1700, 1577.

PMOAVE-Silver Salt . The polymer prepared as described above (500 mg, 0.0795 mmol) was dissolved in 70 mL of heptane and added to 30 mL of EtOH. Silver

acetate (132 mg, 0.795 mmol) was added to the reaction as a solid. The reaction was stirred at room temperature in the dark for 48 h. Water (10 mL) was added to the reaction to separate the layers. The reaction was transferred to a separatory funnel and the aqueous layer was removed. The organic layer was filtered and dried to give 400 mg (79%) of a dark yellow powder. IR (KBr, cm^{-1}): 1698, 1646, 1585.

Latent Biphasic Heck Catalysis. The catalyst used and the procedure was identical to the normal thermomorphic procedure previously described with the difference being that the starting solution was a single phase.³

Latent Biphasic Oxazoline Synthesis. The polymeric Ag(I) catalyst prepared above (125 mg, 0.02 mmol of Ag) was dissolved in 20 mL of heptane. Benzaldehyde (212 mg, 2 mmol), ethyl isocyanoacetate (226 mg, 2 mmol), and Hunig's base (35 μL , 0.2 mmol) were dissolved in 10 mL EtOH containing 1 mmol dodecane as an internal standard. The alcoholic solution was added to the solution of polymer forming a homogeneous system. The reaction was protected from light and stirred at room temperature overnight. At this point, 15 drops (~600 mg) of water were added to induce separation of the layers. The lower layer was removed and stored for metal analysis. A fresh solution of reagents in ethanol was added to the reaction flask. An additional 5 mL of heptane was also added to return the system to a single phase.

Sequestration of Primary Amines by a Heptane-Soluble Polymer Under Latent Biphasic Conditions. In a typical reaction, 2 mmol of a primary amine and 70 μL of propylene oxide (1 mmol) were dissolved in 10 mL of ethanol and heated at 70 °C for 2 h. Then 10 mL of a heptane solution of 1.25 g of the polymer sequesterant PMAOVE (3 mmol) was added to this solution. After stirring 10 min, this miscible mixture of

product, sequestered excess amine and polymer was induced to phase separate into two phases by the addition of 1.5 mL of water. While sequestration of primary amines in the heptane-soluble polymer was quantitative, the aminoalcohol products from longer chain amines (e.g. octyl amine) had some solubility in the heptane phase. In these cases, the nonpolar phase was extracted with aqueous ethanol to completely recover the product. Yields of aminoalcohol products were typically in the range of 80-95% (GC yields). The absence of any contaminating primary amine in the aminoalcohol product was verified by GC chromatography using dodecane as an internal standard.

References

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