

Supporting Information

Reassessing Helical Polycarbodiimide Regioregularity Using Solution

Infrared Spectroscopy

Justin G. Kennemur, Joseph D. DeSousa, James D. Martin, and Bruce M. Novak*

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I. Characterization of Catalysts:

Successful synthesis of was performed and confirmed by reference to previously reported literature.

(R)-BINOL-titanium(IV)-diisopropoxide¹ (98% Yield)

¹H NMR (300 MHz, CDCl₃ stored over molecular sieves) δ (ppm): 1.06 (d, 12H), 4.49 (m, 2H), 6.75 (d, 2H), 7.15 (d, 2H), 7.34 (m, 4H), 7.46 (d, 2H), 7.86 (d, 2H).

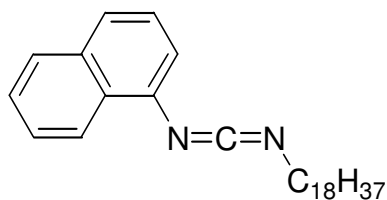
Trichloro-titanium(IV)-(2,2,2-trifluoroethoxide)² (29% Yield)

¹H NMR (300 MHz, toluene-d₈ stored over molecular sieves) δ (ppm): 3.76 (br).

II. Characterization of Monomers:

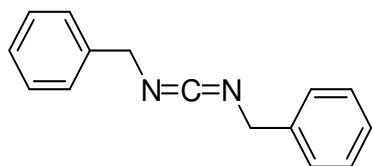
N-(1-naphthyl)-*N'*-(n-octadecyl)carbodiimide (Mono-1)

This monomer was prepared exactly as described in previous literature.³



Yield: 83 %. m.p.: 6 – 8 °C. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 0.86 (t, 3H), 1.24 (br, 28H), 1.43 (m, 2H), 1.71 (m, 2H), 3.45 (t, 2H), 7.28 (d, 1H), 7.38 (t, 1H), 7.48 (m, 2H), 7.59 (d, 1H), 7.79 (m, 1H), 8.26 (m, 1H). ^{13}C -NMR (75 MHz, CDCl_3) δ (ppm): 14.4, 23.0, 27.0, 29.9, 29.6, 29.8 (overlapped), 29.9 (br, overlapped), 31.7, 32.1, 47.1, 119.8, 123.8, 124.6, 126.0 (overlapped), 126.6, 128.0, 129.1, 134.6, 135.8, 137.5. IR(cm^{-1}): 3052.3 (m, C-H aryl), 2926.5 (vs, C-H alkyl), 2853.7 (s, C-H alkyl) 2134.8 (vs, N=C=N). 1575 (s, C=C aryl). HRMS-ESI: $M_{\text{theoretical}} = 420.35045$, $M_{\text{sample}} = 420.34974$, $\Delta M = 0.71$ mmass units (1.70 ppm), $\text{C}_{29}\text{H}_{44}\text{N}_2$.

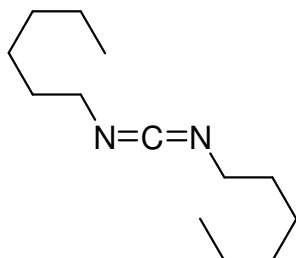
***N,N'*-dibenzylcarbodiimide (Mono-2)**



To a 500 mL round bottom flask 350 mL of dichloromethane was added along with an oval stir bar. To the solvent 10.35 g (63.9 mmol, 1.0 eq) of 1,1'-carbonyldiimidazole was added. To the reaction solution 13.67 g (127.8 mmol, 2.0 eq) of benzylamine was mixed with an equal portion of DCM and added drop wise at room temperature over 30 minutes. Once the addition was complete, reaction solution stirred overnight (~12 hours). DCM was removed via reduced pressure evaporation and the remaining white solids were crystallized from ethanol. Yield: 10.69 g (43.8 mmol) white, sharp, needle-shaped crystals (69 % Yield). To an oven dry 500 mL round bottom flask 10 mL of dichloromethane, 6.33 grams (14.99 mmol) of triphenylphosphine dibromide and a stir bar. The solution was then cooled in an ice bath to 0 °C. To the slurry 4.32 mL (3.2 g, 31.23 mmol) triethylamine was added drop wise. Following the addition of the triethylamine, 3.0 g (12.5 mmol) *N,N'*-dibenzylurea was added in three equal portion over a one hour period. Once the addition was complete the reaction continued at 0 °C for two hours. To the reaction solution 300 mL portion of pentane was added and the precipitated solids were filtered; the solvent removed by reduced pressure evaporation. A second portion of pentane was added followed by a second filtration. Remaining solvent was removed by reduced pressure evaporation. Final purification was done by column chromatography with silica gel as the stationary phase and DCM as the mobile phase.

Yield: yellow oil, 65.1 %. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.34 – 7.20 (m, 6H), 7.18 (d, 4H), 4.30 (s, 4H). IR (cm^{-1}): 3062 (m, C-H aryl), 3030 (m, C-H aryl), 2933 (m, C-H alkyl), 2127 (vs, N=C=N). HRMS-ESI (m/z): $M_{\text{theoretical}} = 223.1223$, $M_{\text{sample}} = 223.1232$, $\Delta M = -0.19$ mmass units (-0.87 ppm) $\text{C}_{15}\text{H}_{14}\text{N}_2$.

***N,N'*-di(n-hexyl)carbodiimide (Mono-3)**

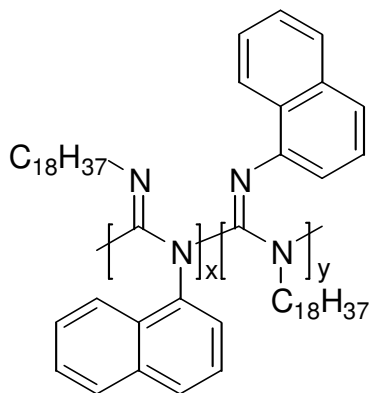


This monomer was made in accordance to previously reported procedures by our group⁴⁻⁷ but, for clarity, will be described here. 4.201 g (33 mmol) of hexyl isocyanate was diluted in 25 mL of DCM in a 250 mL round bottom flask with a stir bar and cooled to 0 °C in an ice bath. 3.336 g (33 mmol) of hexylamine was diluted in 25 mL of DCM and added to a pressure equalizing addition funnel. The hexylamine solution was added slowly to the cool isocyanate solution and once fully added the solution was allowed to stir at 0 °C for 1 hour and then room temperature for another hour. DCM was removed from the reaction solution by rotary evaporation leaving a crude white residue which was purified by recrystallization in EtOH. Following aspiration filtration and full drying by vacuum, the urea was recovered as a white solid (80 % Yield). To a clean 500 mL round bottom flask, 6.8756 g (26 mmol) of triphenylphosphine was dissolved in 10 mL of DCM and cooled to 0 °C using an ice bath. 1.35 mL (26 mmol) of Br_2 was diluted in 15 mL of DCM and added to a pressure equalizing addition funnel. The Br_2 solution was slowly added to the PPh_3 solution resulting in a yellow-white slurry. 7.81 mL (56 mmol) of TEA was then added to the slurry. Keeping the charged solution cool at 0 °C, 5.498 g (24 mmol) of urea was dissolved in 15 mL of DCM and added to the charged solution dropwise by addition funnel. The ice bath was allowed to slowly deplete overnight. A nitrogen blanket was applied throughout this process to prevent water condensation within the reaction flask. The following morning the reaction was quenched with ~200 mL of hexanes and the precipitates were filtered. The filtrate was reduced by rotary evaporation yielding a salty oil residue. The hexanes quenching cycle was repeated and the resulting oil was vacuum distilled at 65 °C (200 mtorr), to yield a colorless oil.

Yield 66% (after vacuum distillation) $^1\text{H NMR}$ (300 MHz, CDCl_3) δ (ppm): 0.89 (t, 6H), 1.25 – 1.40 (m, 12H), 1.57 (m, 4H), 3.19 (t, 4H). IR(cm^{-1}): 2930 (vs, C-H alkyl), 2859 (s, C-H alkyl), 2131 (vs, N=C=N). HRMS-ESI: $M_{\text{theoretical}} = 211.2169$, $M_{\text{sample}} = 211.2169$, $\Delta M = -0.06$ mmass units (-0.27 ppm), $\text{C}_{13}\text{H}_{26}\text{N}_2$.

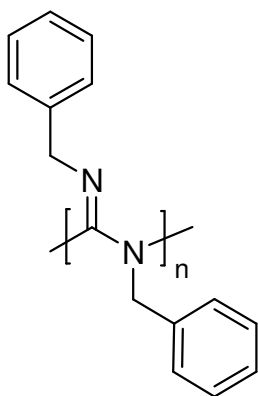
III. Characterization of Polymers:

Poly-*N*-(1-naphthyl)-*N'*-(*n*-octadecyl)carbodiimide (Poly-1)
was previously reported and characterized.³



Monomer:Catalyst (molar ratio) 215:1. Yield: 88 %. $M_w = 78,000$, $M_w/M_n = 4.2$.
 ^1H NMR (300 MHz, CDCl_3) δ (ppm): (0.66, 0.88, 1.00, 1.26, 1.53) (br, overlapping), (7.39, 7.15, 7.01, 6.56, 6.43) (broad overlapping). IR thin film (cm^{-1}): 3046 (m, C-H aryl), 2923 (vs, C-H alkyl), 2852 (s, C-H alkyl), 1641 (s, C=N aryl), 1619 (s, C=N alkyl), 1586 (m, C=C aryl).

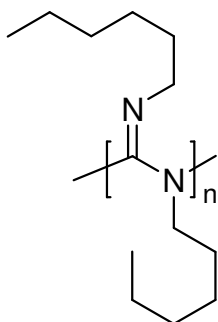
Poly-*N,N'*-dibenzylcarbodiimide (Poly-2)



To a clean, dry 20 mL vial 2.14 g (9.63 mmol, 150 eq.) *N,N'*-dibenzylcarbodiimide was added with a magnetic stir bar. To the monomer 0.67 mL of a 24.4 mg/mL solution of Trichloro-titanium(IV)-(2,2,2-trifluoroethoxide) (0.0163 g, 0.0642 mmol, 1.0 eq.) in dry chloroform was added to the monomer. After 1 hour the polymerization seized the stir bar. The reaction was terminated at the end of 96 hours. The solid polymer was dissolved in 7 mL of chloroform and precipitated in to 300 mL of methanol. The solids were filtered and dried. Monomer:Catalyst (molar ratio) 150:1 Yield: 1.55 grams (6.97 mmol)

off-white solid, 72.4 %. IR KBr pellet (cm^{-1}): 3080 (m, C-H aryl), 3061 (m, C-H aryl), 3028 (m, C-H aryl), 2972 (m, C-H alkyl), 2899 (m, C-H alkyl), 1649 (s, C=N aryl), 1628 (s, C=N aryl), 1590 (m, C=C aryl). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.05 – 6.49 (Ar-H, 10H, very broad triplet), 5.41 (benzyl-H, 1H, broad singlet), 4.45 (benzyl-H, 1H, broad singlet), 4.00 (benzyl-H, $J = 14.8$, 1H, broad doublet), 3.57 (benzyl-H, $J = 14.8$, 1H, broad doublet).

Poly-*N,N'*-di(*n*-hexyl)carbodiimide (Poly-3)



To a clean, dry 20 mL vial 1.27 g (6.02 mmol, 126 eq.) *N,N'*-di-*n*-hexylcarbodiimide was added with a magnetic stir bar. To the monomer 1.00 mL of a 12.1 mg/mL solution of Trichloro-titanium(IV)-(2,2,2-trifluoroethoxide) (0.0121 g, 0.0478 mmol, 1.0 eq.) in dry DCM was added to the monomer. After 1 hour the polymerization seized the stir bar. The reaction was terminated at the end of 96 hours. The solid polymer was dissolved in 7 mL of chloroform and precipitated in to 300 mL of methanol. The solids were filtered and dried. Monomer:Catalyst (molar ratio) 126:1 Yield: 0.89 grams (4.22 mmol) white solid, 70 %. IR KBr thin film (cm^{-1}): 2954 (s, C-H alkyl), 2927 (s, C-H alkyl), 2856 (s, C-H alkyl), 1645 (s, C=N). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 3.15, (broad quartet), (1.47, 1.29, 0.89) (broad overlapping).

VI. References:

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