

Accessory Publication

Searching for Stars: Selective desulfurization and fluorescence spectroscopy as new tools in the search for cross-termination side-products in Reversible Addition Fragmentation chain Transfer (RAFT) polymerization

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EXPERIMENTAL

Materials

Carbazole was purchased from Alfa Aesar (96%) and used without further purification. Sodium hydride was purchased from Sigma Aldrich as a 60 % (w/w) dispersion in mineral oil. Dodecyl bromide, benzyl bromide, potassium hydroxide and carbon disulphide were purchased from Sigma Aldrich and used without further purification. Styrene (99%) was obtained from Sigma Aldrich and purified from the stabiliser by passing through an alumina column prior to use. AIBN was obtained from Wako fine chemicals and was recrystallised from methanol before use. Raney Nickel was purchased as a slurry in water from Sigma Aldrich. Chloroform (HPLC grade) was passed through a column of alumina before use in fluorescence experiments.

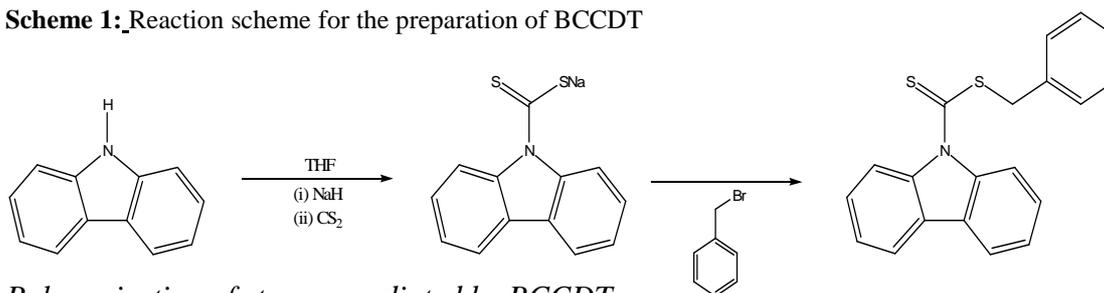
Synthesis of BCCDT

All apparatus was flame dried under vacuum prior to reaction. Sodium hydride in mineral oil (60 % (w/w)) (2.87 g, 71.8 mmol[†]) was added to a dry 3 neck round bottomed flask containing a magnetic stirring bar, under nitrogen. Hexane (50 ml) was added and the mixture was allowed to stir for 5 minutes to disperse the sodium hydride in the hexane and dissolve the mineral oil. The hexane/mineral oil solution was drawn off and discarded. This process was repeated a further 2 times to leave pure sodium hydride as a clean white powder. A solution of carbazole (1) (10 g, 59.8 mmol) in tetrahydrofuran (THF) was added to a pressure equalising dropping funnel sitting atop the 3 neck round bottomed flask containing the purified sodium hydride. The 3 necked round bottomed flask was fitted with a water condenser containing a gas collection balloon. The carbazole was added to the sodium hydride over ice and the balloon was purged regularly to relieve the build up of hydrogen gas. After 30 minutes of stirring all the hydrogen had been evolved and the contents of the flask

were heated to 60°C for 60 minutes. The reaction mixture was then cooled to 3°C and carbon disulphide (9.18 g, 119.6 mmol) was added to the reaction mixture drop wise over a period of 30 minutes and allowed to come to room temperature and stirred for 2 hours. The contents of the flask were then raised to 60°C for 2 hours to remove the excess carbon disulphide before the next step. Benzyl bromide (10.7 g, 62.8 mmol) was added and the mixture was brought to reflux for 12 hours (see Scheme 1). The reaction mixture was reduced by rotary evaporation and BCCDT (3) was recrystallised from boiling methanol as a bright yellow crystalline solid.

¹H NMR (300 MHz, CDCl₃): δ=8.44–8.48 (d, 2H, carbazole–H), 7.89–8.01 (d, 2H, carbazole–H), 7.33–7.48 (m, 7H, carbazole–H and Ar–H), 4.73 (s, 2H, –CH₂–Ar).

Scheme 1: Reaction scheme for the preparation of BCCDT



Polymerization of styrene mediated by BCCDT

In each case (Sty1–Sty3) a 10 ml stock solution of styrene, BCCDT and AIBN was prepared with the reagent concentrations shown in Table 1, and from these stock solutions 1.5 ml of the solution was decanted and added to a 2 ml glass vial, representing each kinetic point. The vial was then stoppered with a suba seal and wrapped with parafilm® and added to a water ice slurry and deoxygenated with nitrogen for 5 minutes. The vial was then added to a pre-heated oil bath at 60°C for the duration of the polymerization. At predetermined times the vials were removed from the oil bath and immersed in ice water to effectively halt the reaction. Monomer conversion was calculated by ¹H NMR in CDCl₃ on a Brüker 400MHz instrument. Molecular weight and molecular weight evolution was calculated by size exclusion chromatography (SEC) on a Polymer Laboratories instrument fitted with two mixed C columns and a guard column. Detection was by refractive index calibrated with poly(styrene) standards. THF was used as the eluent containing 0.05% toluene as a flow rate marker. The flowrate was run at 1 ml/min.

Table 1: Reagent concentration used in the polymerisation of styrene to determine a retardation effect

Sample	Styrene g, mmol	BCCDT mg, mmol	AIBN mg, mmol	Molar Ratio of Styrene:BCCDT:AIBN
Sty1	9.921, 95	63.5, 0.19	15.6, 0.095	500:1:0.5
Sty2	9.616, 92	307.9, 0.92	75.8, 0.46	100:1:0.5
Sty3	9.675, 93	310, 0.93	15.3, 0.093	100:1:0.1

Simulations with FORTRAN 90 Code

A code was written to simulate the conversion and estimate the concentration of three-armed stars in BCCDT mediated polymerisation of styrene. The following parameters were used in the simulation.

Monomer Concentration	8.4 mol/L
Temperature	60°C
k_d Arrhenius	$2.890e^{15} 1.302e^5$
f constant	$7.000e^{-1}$
k_i constant	$4.000e^3$
kreini constant	$1.000e^3$
k_p constant	$3.300e^2$
k_t function	$1.000e^8 l^{-0.25}$
$k_{ad,1}$ constant	$4.000e^6$
$k_{\beta,1}$ constant	$1.00e^4$
$K_{ad,2}$ constant	$4.000e^6$
$K_{\beta,2}$ constant	$1.00e^4$
k_{ad} constant	$4.000e^6$
k_{β} constant	$1.00e^4$
$K_{t,cross 1}$ constant	$5.000e^8$
$K_{t,cross}$ constant	$0.5 * k_t$

In this case l is the chain length as determined from conversion. It is interesting that a termination rate coefficient of 10^8 was needed to fit the conversion data, which is somewhat lower than expected from *a priori* arguments, however, this value is still consistent as an extrapolation of the long chain termination rate to short chain lengths. [REFS]

Predici Calculations

Simulations of the rate of polymerisation of styrene mediated by BCCDT were performed using the following values and rate coefficient estimates:

Monomer Concentration	8.4 mol/L
Temperature	60°C
k_d Arrhenius	$2.890e^{15} 1.302e^5$
f constant	$7.000e^{-1}$
k_i constant	$1.000e^3$
kreini constant	$1.000e^3$
k_p constant	$3.300e^2$
k_t function	$1.000e^{8*(1-X^{0.25})}$
$k_{ad,1}$ constant	$4.000e^6$
$k_{\beta,1}$ constant	$7.000e^4$
$K_{ad,2}$ constant	$4.000e^6$
$K_{\beta,2}$ constant	$7.000e^4$
k_{ad} constant	$4.000e^6$
k_{β} constant	$7.000e^4$
$K_{t,cross 1}$ constant	$5.000e^8$
$K_{t,cross}$ constant	$0.5 * k_t$

Figure 1: Conversion as predicted by PREDICI[®] simulations.

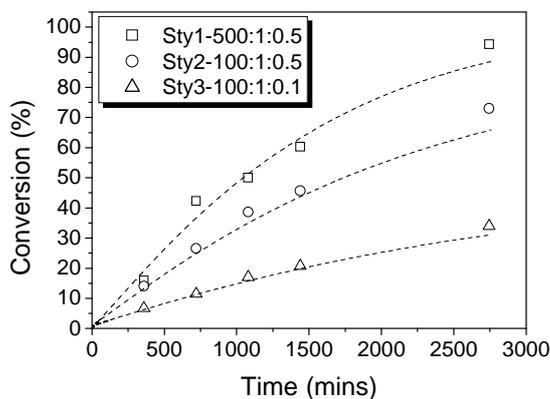
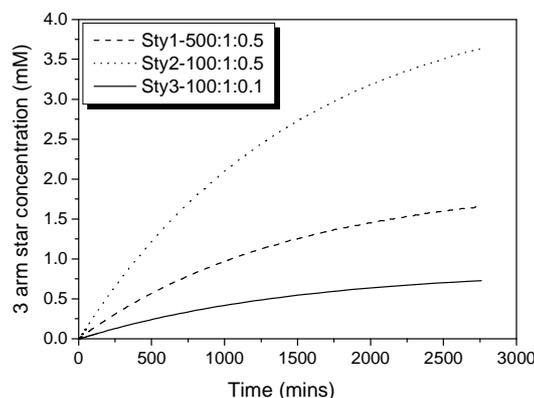


Figure 2: Three-armed stars predicted by PREDICI[®] simulation



Both our simulation and the PREDICI[®] simulations gave three armed star concentrations within a factor of 5. Differences in the concentration could be due to differences in the assumptions about the cross termination rate or due to the variations in the fitted addition and fragmentation rates.

Simulation of the conversion with the Oligomer Termination Model

This section models the conversion and only allows short chains to participate in the reaction. In this section we only consider the AIBN fragments and leaving group radicals to cross-terminate. This is the same as in our earlier paper. This accounts for the absence of three armed stars post Raney nickel reduction, since the third arm is sufficiently short that it will not be precipitated out of solution. The following parameters were used to model the conversion.

Monomer Concentration	8.4 mol/L
Temperature	60°C
k_d Arrhenius	$2.890e^{15} \ 1.302e^5$
f constant	$7.000e^{-1}$
k_i constant	$4.000e^3$
kreini constant	$6.000e^2$
k_p constant	$3.500e^2$
k_t function	$1.000e^8 \ T^{-0.16}$
$k_{ad,1}$ constant	$4.000e^6$
$k_{\beta,1}$ constant	$1.000e^3$
$k_{ad,2}$ constant	$4.000e^6$
$k_{\beta,2}$ constant	$1.000e^3$
k_{ad} constant	$4.000e^6$
k_{β} constant	$1.1000e^1$
$k_{t,cross \ 1}$ constant	$5.000e^7$
$k_{t,cross}$ constant (Long-Chain)	0

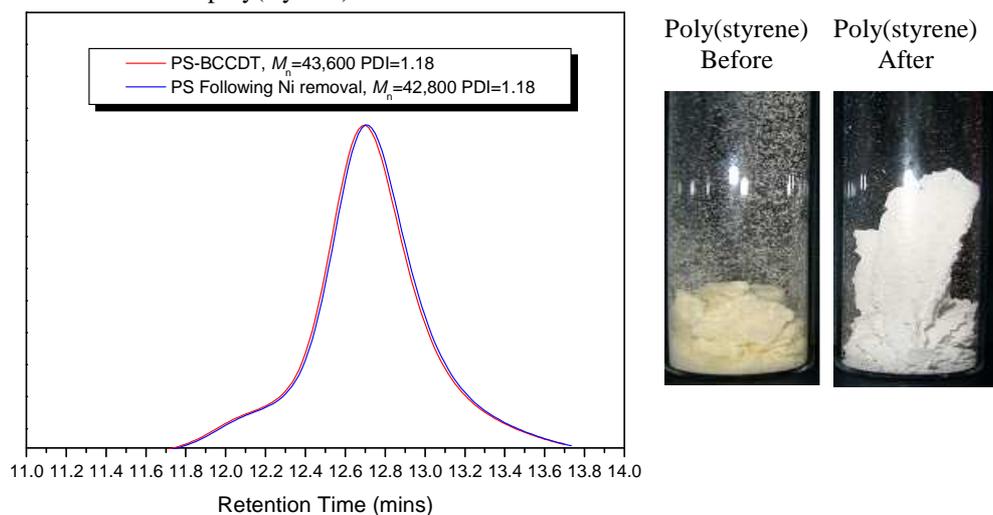
Nickel reduction of poly(styryl)-BCCDT

Poly(styryl)-BCCDT (2 g, $M_n = 43,600$ g/mol, PDI=1.18) was dissolved in THF (10ml) in a 2 neck round bottomed flask attached with water condenser and pressure equalising dropping funnel. A large excess of NiAl alloy (200 mg, 1.15 mmol of nickel) was added and the flask was immersed in an ice bath. A 2M NaOH solution (30 ml) was added to the separating funnel and added drop wise to the mixture, slowly, over 30 mins, with strong effervescence and the liberation of hydrogen gas. The contents of the flask were brought to room temperature and then slowly raised to 90°C and held at this temperature for 15 hours, over stirring. Following reaction, the contents of the flask were filtered through a two inch bed of cellite to remove the catalyst and washed thoroughly with THF to ensure complete recovery of the polymer. The polymer was reconstituted through rotary evaporation, and precipitation from THF into an excess of cold hexane to give white, decoloured poly(styrene).

Molecular weight comparisons of poly(styrene) prior to and following nickel reduction

Following the nickel reduction, the polymer was found to change from a yellow coloured poly(styrene) (due to the end group) to white poly(styrene). The molecular weight and the PDI of the newly acquired material was determined and compared with that before the reduction, as shown in Figure 3.

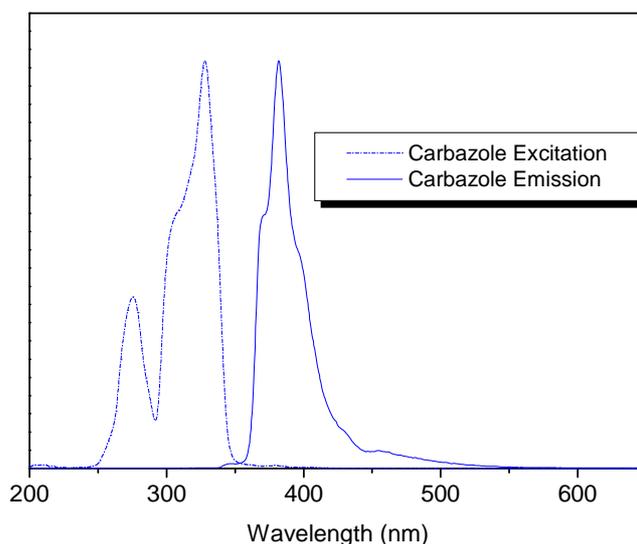
Figure 3: GPC traces of poly(styrene) before and after nickel reduction



Fluorescence spectroscopy

All fluorescence experiments were performed on a Perkin Elmer LS55 Spectrofluorimeter and were ran using chloroform as the solvent. The chloroform was dried and purified by passing through a large column of basic alumina prior to use. Figure 4 shows the typical excitation-emission spectra of carbazole at 1×10^{-5} M, in chloroform.

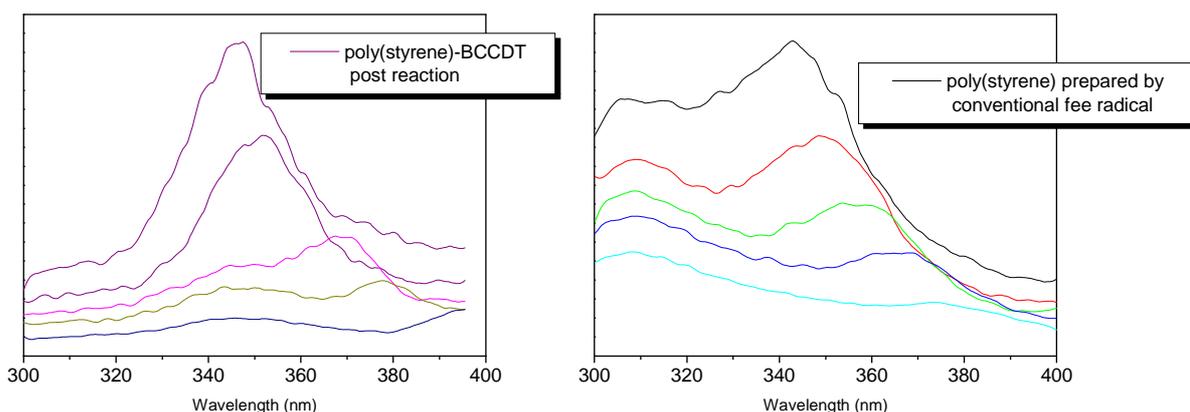
Figure 4: Excitation-Emission Spectra of Carbazole



Following nickel reduction, poly(styrene) was dissolved in chloroform (10 ml) for fluorescence analysis. A pre-scan function was performed on the sample to give the λ_{\max} of absorption and the emission wavelength. An emission at 348 nm was revealed and it initially appeared that we had found evidence of star formation. In order to prove, however, that the signal was due to fluorescence we then increased the excitation wavelength in increments of 2 nm and monitored the excitation spectra.

From Figure 5 it can be seen clearly that the excitation spectra changes and shifts to the right; to higher wavelengths, indicative of a raman signal, and not fluorescence. The fluorescence spectra from pure poly(styrene) (Figure 5) prepared by conventional free radical polymerization in the absence of RAFT agent reveals an almost identical series of curves convincing us that there are no stars detectable in our system.

Figure 5: Fluorescence spectra of poly(styrene)-BCCDT following nickel removal of end group (*left* graph) and the fluorescence spectra of poly(styrene) prepared by conventional free radical polymerization in the absence of RAFT agent (*right* graph).



Nickel reduction of BCCDT.

As the Rainey Nickel catalyst is produced in situ by reaction of NaOH with NiAl, it is important to verify the absence of side reactions between NaOH and the dithiocarbamate yielding to hydrolysis of the thiocarbonyl thio derivative.

BCCDT (200 mg, 0.619 mmol) was dissolved in toluene (10 ml) and added to a round bottomed flask fitted with a Dean Stark apparatus. A large excess of NiAl alloy (200 mg, 1.15 mmol of nickel) was added and the flask was immersed in an ice bath. A 2M NaOH solution (30 ml) was added to the separating funnel and added drop wise to the mixture, slowly, over 30 mins, with strong effervescence and the liberation of hydrogen gas. The reaction was allowed to continue at reflux for 48 hours. Following reaction, the contents of the flask were filtered through a two inch bed of cellite to remove the catalyst. Analyses revealed the presence of toluene and *N*-methyl carbazole.

Preparation of N'-dodecyl carbazole

All apparatus was flame dried under vacuum prior to reaction. Sodium hydride in mineral oil (60 % (w/w)) (2.4 g, 60 mmol) was added to a dry 3 neck round bottomed flask containing a magnetic stirring bar, under nitrogen. Hexane (50 ml) was added and the mixture was allowed to stir for 5 minutes to disperse the sodium hydride in the hexane and dissolve the mineral oil. The hexane/mineral oil solution was drawn off and discarded. This process was repeated a further 2 times to leave pure sodium hydride as a clean white powder. A solution of carbazole (8.35 g, 50 mmol) in tetrahydrofuran (THF) was added to a pressure equalising dropping funnel sitting atop the 3 neck round bottomed flask containing the purified sodium hydride. The 3 necked round bottomed flask was fitted with a water condenser containing a gas collection balloon. The carbazole was added to the sodium hydride over ice and the balloon was purged regularly to relieve the build up of hydrogen gas. After 30

minutes of stirring all the hydrogen had been evolved and the contents of the flask were heated to 60°C for 60 minutes. 1-bromododecane (12.46 g, 50 mmol) was added to the reaction mixture and the contents of the flask were held at 60°C for 15 hours. The contents of the flask was added to a large separating funnel along with deionised water (150 ml) and dichloromethane (150 ml) and N'-dodecyl carbazole was extracted into the organic layer and reduced *via* rotary evaporation and purified on a column of silica (98:2, Hexane:Diethyl ether) to give an oily yellow liquid in 93 % yield.

Nickel Reduction reaction on NDDC

NDDC (5g, 14.9 mmol) was dissolved in THF (100ml) in a 2 neck round bottomed flask attached with water condenser and pressure equalising dropping funnel. A large excess of NiAl alloy (25.91 g, 149 mmol of nickel) was added and the flask was immersed in an ice bath. A 2M NaOH solution (300 ml) was added to the separating funnel and added drop wise to the mixture, slowly, over 30 mins, with strong effervescence and the liberation of hydrogen gas (see Scheme 2). The contents of the flask were brought to room temperature and then slowly raised to 90°C and held at this temperature for 15 hours. Following reaction, the contents of the flask were filtered through a four inch bed of cellite to remove the catalyst and washed thoroughly with THF to ensure complete recovery of the NDDC. Following filtration through cellite, and removal of solvents, the material taken forward for analysis with no further purification. It can be seen from Figures 6 and 7 that the ¹H and ¹³C spectra for NDDC prior to and following the Raney nickel reduction remain entirely unchanged. Furthermore, the absorption and emission spectras of NDDC before and after reaction remain virtually unchanged proving to us that the conditions of Raney nickel reduction have no effect on any nitrogen-carbon bonds in our system and would not detriment any 3 arm stars created during the polymerization.

Scheme 2: Reaction scheme for the preparation of N'-dodecyl carbazole

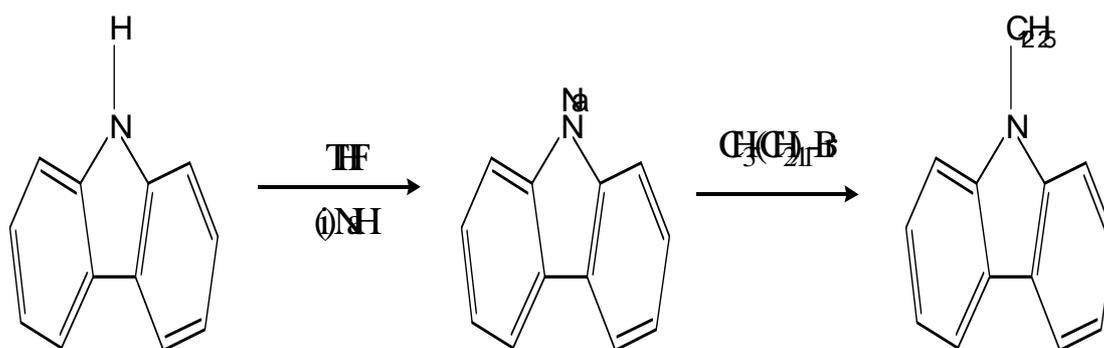


Figure 6: ^1H NMR spectra of NDDC before (*top*) and following (*bottom*) nickel reduction conditions

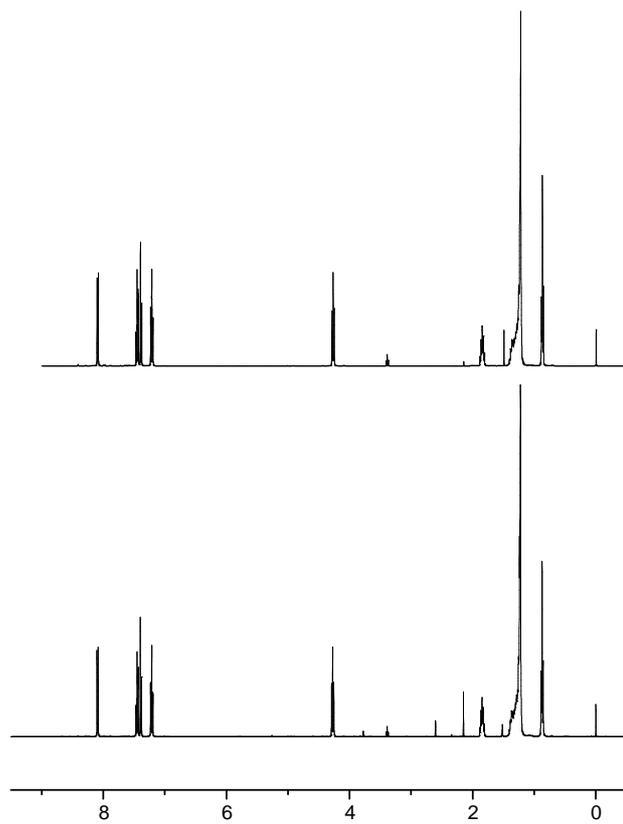


Figure 7: ^{13}C NMR spectra of NDDC before (*top*) and following (*bottom*) nickel reduction conditions

