

Sequestration of Dyes from Water into Poly(α -olefins) Using Polyisobutylene Sequestering Agents

Neil Rosenfeld, Mara P. Alonso, Courtney Humphries and David E. Bergbreiter *

Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

* Correspondence: bergbreiter@tamu.edu

General information

Poly-(α -olefin)s (PAOs) including a PAO with a molecular weight of 432 Da was provided by Exxon Mobil. Alkene terminated polyisobutylene (PIB) with a reported molecular weight (M_n) of 450, 1000, and 2300 Da was obtained from Texas Polymer Corporation (TPC) and/or BASF [1,2]. All other reagents and solvents were purchased from commercial sources. ^1H NMR spectra were recorded on Bruker NMR spectrometers operating at 400 MHz, and chemical shifts were reported in ppm with reference to CDCl_3 at 7.26 ppm. ^{13}C NMR spectra were recorded on Bruker NMR spectrometers operating at 100 MHz. Chemical shifts are reported in ppm with reference to CDCl_3 at 77.00 ppm. UV-Vis spectra were obtained on a Shimadzu UV-2700 spectrophotometer.

The preparation of PIB-OH from PIB-alkene, and the preparation of PIB-I from PIB-OH are detailed in reference [3]. The preparation of PIB-imidazole and PIB- NEt_2 are detailed in reference [4]. Additionally, the synthesis of PIB-acac- CF_3 was detailed in reference [5].

Preparation of PIB-ammonium and imidazolium salts (1 and 2)

PIB₂₃₀₀-ammonium and imidazolium salts **1** and **2** were both prepared by an $\text{S}_{\text{N}}2$ substitution reaction under similar conditions. 1 g of PIB₂₃₀₀-imidazole or - NEt_2 (0.5 mmol) was dissolved in 5 mL of DCM in a vial. The DCM solution was then combined with (3 mmol) of Me-I or *n*Bu-I and stirred overnight at room temperature. The solution was then concentrated under reduced pressure and the product (**1** or **2**) was used without the need for further purification. The product was collected in a 99% yield (1.0 g)

PIB₂₃₀₀-diethyl-methyl ammonium iodide (**1**): ^1H NMR (400 MHz, CDCl_3) δ 3.6-3.8 (m, 4H), 3.39 (dd, J = 13.1, 6.6 Hz, 1H), 3.30 (s, 3H), 3.20 (dd, J = 12.1, 3.2 Hz, 1H), 1.60-1.00 (m, 414H). ^{13}C NMR (100 MHz, CDCl_3) δ : 8.8, 14.3, multiple peaks between 20.9 and 38.4, 49.0, 53.4, multiple peaks between 57.3 and 59.8, 69.7.

PIB₂₃₀₀-butyl imidazolium (**2**): ^1H NMR (400 MHz, CDCl_3) δ 10.6 (s, 1H), 7.2 (s, 2H), 4.2 (m, 4H), 1.6-1.0 (m, 414H). ^{13}C NMR (100 MHz, CDCl_3) δ : 2.0, 6.8, 12.8, multiple peaks between 20 and 40, 50 and 60, 116.2, 121.5.

Preparation of PIB-imidazolium salt (3)

5 mmol (11.5 g) of PIB₂₃₀₀-I was dissolved in 100 mL of anisole in a round bottomed flask. Then, 5.0 g (20 mmol) of 1-butyl-2-(2,6-dimethylphenyl)-4,5-dimethyl-1H-imidazole was added to this anisole

solution [6]. The anisole solution was then refluxed for 96 h. Once the reaction was complete, 100 mL of hexanes was added to this mixture. The hexane phase was then added to a separatory funnel and extracted 3 x with 2 M HCl. The upper hexane and lower HCl phases were centrifuged to separate emulsions that had formed during the liquid-liquid extraction. The hexane phase was then dried over Na₂SO₄, and then concentrated under reduced pressure. This crude residue was then purified by silica gel column chromatography using DCM/MeOH as the eluent. The product was collected in a 50% yield (6 g).

PIB₂₃₀₀-Coates imidazolium iodide (**3**): ¹H NMR (400 MHz, CDCl₃) δ 7.49 (t, J = 7.8 Hz, 1H), 7.29 (t, J = 7.3 Hz, 2H), 4.04 (m, 1H), 3.81 (m, 1H), 3.67 (d, J = 8.28 Hz, 2H); 2.57 (s, 3H), 2.48 (s, 3H), 2.17 (s, 3H), 2.15 (s, 3H), 1-1.4 (m, 296H), 0.86 (t, J = 7.35 Hz, 3H), 0.61 (d, J = 4.90 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 142.13, 138.94, 132.88, 129.23, 129.02, 128.06, 127.61, 121.64, 118.83 (multiple poorly resolved peaks between 60-50, 40-20). FT-IR (-cm, neat): 2982, 2949, 2893, 1466, 1389, 1366, 1231, 770.

General procedure for the extraction of dyes from water

Solution of PIB-ammonium or imidazolium iodide (**1** – **3**) in PAO₄₃₂ were prepared at various concentrations. Then, 5 mL of a pH 10 aqueous phase containing the dye of interest was added to a centrifuge tube along with 0.5 g of the PAO solution. The mixture was vortex-mixed for either 2, 5, or 10 min at 3000 rpm and then centrifuged for 15 min at 3000 rpm. Initial experiments simply used visual observation that showed the water phase became colorless. Subsequently, the lower aqueous phase was analyzed by UV-Vis spectroscopy, and its absorbance was recorded at λ_{max}. This absorbance value was compared to the absorbance of the virgin dye solution in water prior to extraction. Dye concentrations were determined gravimetrically. In instances where the virgin dye solution's absorbance was >1.5, ¹H NMR spectroscopic analysis was used too to determine dye concentration before and after extraction [7]. To carry out this experiment, a solution of a methoxy-terminated polyethylene glycol (M_n = 2000) standard was prepared in D₂O at a concentration of 1000 mg/L, and 0.5 g of this solution was combined with 0.5 g of the extracted aqueous phase. This D₂O/H₂O mixture solution was then analyzed by ¹H NMR spectroscopy using the WATERGATE protocol. The amount of dye contaminant was quantified by integrating the dye contaminant peaks with respect to the integral of the ¹³C satellite peaks for the methoxy -CH₃ singlet and/or the -CH₂CH₂O- satellite peak [7].

Determination of extraction efficiency using UV-Visible Spectroscopy

When absorbance (A) was used to determine extraction efficiency, Equation S1 was applied.

$$\text{Extraction Efficiency} = \frac{\text{Absorbance of extracted aqueous phase}}{\text{Absorbance of virgin dye solution}} \times 100 \quad \text{Equation S1}$$

For example, in an experiment where phenolphthalein was extracted from a pH 10 aqueous phase into a PAO₄₃₂ solution containing sequestering agent **3**:

$$\text{Extraction Efficiency} = \frac{0.11}{0.95} \times 100 = 88 \%$$

Determination of extraction efficiency using ^1H NMR spectroscopic analysis

When dye concentrations were too high for UV-Visible spectrophotometric analysis, ^1H NMR spectroscopic analysis of dye concentrations was carried out using an mPEG internal standard [4,7]. Equation S2 was applied in this context to determine the concentration of dyes in water (mg/kg).

$$\begin{aligned} \frac{\text{mg mPEG}}{\text{kg D}_2\text{O}} \times \frac{1 \text{ mmol mPEG}}{2000 \text{ mg mPEG}} \times \frac{3 \text{ methoxy H}}{1 \text{ mmol mPEG}} \times \frac{\text{integral of impurity}}{100 \text{ integral of methoxy}} \\ \times \frac{1 \text{ mmol impurity}}{\# \text{ of H integrated for impurity}} \times \frac{\text{mg impurity}}{1 \text{ mmol impurity}} = \frac{\text{mg impurity}}{\text{kg water}} \end{aligned} \quad \text{Equation S2}$$

For example, in an experiment where methylene blue was extracted from an aqueous solution into a PAO₄₃₂ solution containing sequestering agent **4**, the concentration of the virgin dye solution was calculated as follows:

$$\begin{aligned} \frac{1000 \text{ mg mPEG}}{1 \text{ kg D}_2\text{O}} \times \frac{1 \text{ mmol mPEG}}{2000 \text{ mg mPEG}} \times \frac{3 \text{ methoxy H}}{1 \text{ mmol mPEG}} \times \frac{1000 \text{ integral of impurity}}{100 \text{ integral of methoxy}} \\ \times \frac{1 \text{ mmol impurity}}{12 \text{ H integrated for impurity}} \times \frac{320 \text{ mg impurity}}{1 \text{ mmol impurity}} = \frac{400 \text{ mg impurity}}{1 \text{ kg water}} = 400 \text{ mg/kg} \end{aligned}$$

Since methylene blue was not detected by ^1H NMR spectroscopic analysis after extraction using a PAO₄₃₂ solution of **3**, the integral for the impurity was zero. This gives us a concentration of:

$$\begin{aligned} \frac{1000 \text{ mg mPEG}}{1 \text{ kg D}_2\text{O}} \times \frac{1 \text{ mmol mPEG}}{2000 \text{ mg mPEG}} \times \frac{3 \text{ methoxy H}}{1 \text{ mmol mPEG}} \times \frac{0 \text{ integral of impurity}}{100 \text{ integral of methoxy}} \\ \times \frac{1 \text{ mmol impurity}}{12 \text{ H integrated for impurity}} \times \frac{320 \text{ mg impurity}}{1 \text{ mmol impurity}} = \frac{400 \text{ mg impurity}}{1 \text{ kg water}} = 0 \text{ mg/kg} \end{aligned}$$

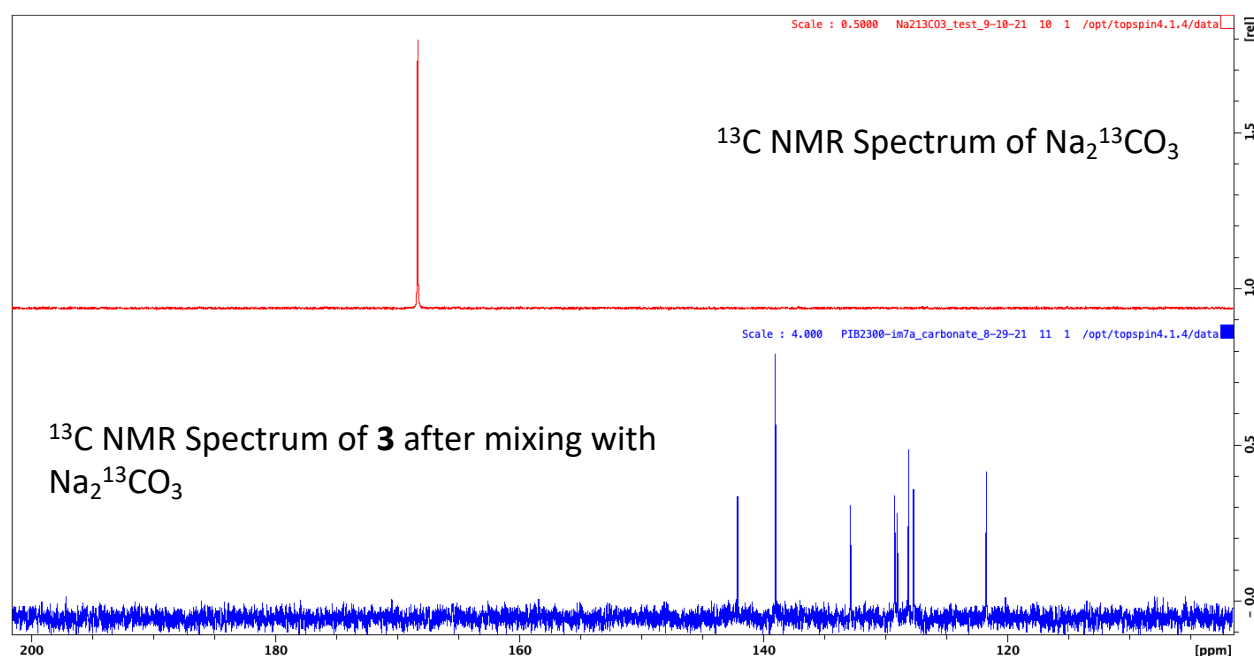
Since spectroscopic analysis fails to detect methylene blue in this extracted solution, we report the final concentration as “not detected.”

Regeneration and recycling of the PAO phase

Solutions were prepared that contained 5 mM of PIB₂₃₀₀-Coate's imidazolium salt (**3**) in PAO₄₃₂. Then 2 mL of this PAO₄₃₂ solution was combined with 5 mL of a pH 10 aqueous phase that contained 0.1 mM of either p-methyl red or dichlorofluorescein. A greater volume of PAO was used in this experiment to facilitate the transfer of PAO from container to container. A larger volume of PAO₄₃₂ was used in this experiment since physical losses in experiments with 0.5 g of PAO would be problematic. The mixture was then vortexed mixed for 10 min at 3000 rpm, then centrifuged for 15 min at 3000 rpm. The lower aqueous phase was analyzed by UV-Vis spectroscopy to determine the concentration of dye after extraction. The upper PAO phase was stirred with 2 drops of CH₃-I to convert the dye anion into either a methyl ester or ether. This regenerated the iodide anion of **3**. At this point the PAO solution of **3** could be reused, and this cycle could be repeated up to 10 times. After the 5th extraction, the PAO solution became cloudy. This solid was determined to be the methyl ester of p-methyl red. After the 5th cycle, care was taken after centrifugation to separate as much of the insoluble solid from the PAO phase as possible before proceeding with the subsequent extraction. A total of 10 sequential extractions were performed using the same, regenerated PAO phase containing **3** as a sequestering agent.

Control for testing if carbonate (CO_3^{2-}) exchanges with I^- counter anion of cationic sequestering agents

To test whether carbonate anions exchange with iodide counteranions of the sequestering agent at any point during extraction, PAO₄₃₂ containing 0.05 M of sequestering agent **3** with the iodide counteranion was stirred over solid $\text{Na}_2^{13}\text{CO}_3$ for 24h. Once complete, the PAO solution was analyzed by ^{13}C spectroscopic analysis for the presence of the ^{13}C resonance of carbonate (at approximately 170 ppm on the ^{13}C NMR spectrum). Spectroscopic analysis of the PAO solution revealed all of the expected signals corresponding with imidazolium cation **3**, with no signal corresponding with the ^{13}C in a carbonate counteranion. Likewise, exchange of the carbonate counteranion was not observed when the PAO₄₃₂ solution containing **3** was mixed with a pH 10 solution containing $\text{Na}_2^{13}\text{CO}_3$.



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