10.1071/CH24085
Australian Journal of Chemistry

Supplementary Material

The quantification of radical concentration in organic radical polymers: techniques and challenges

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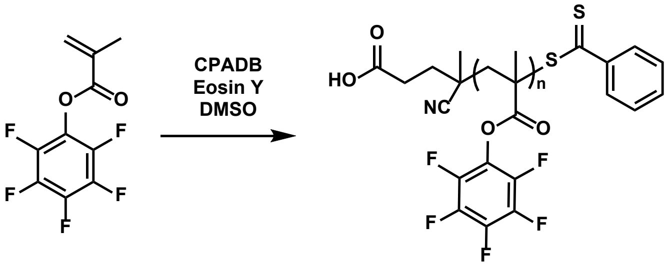
Experimental Details

General experimental

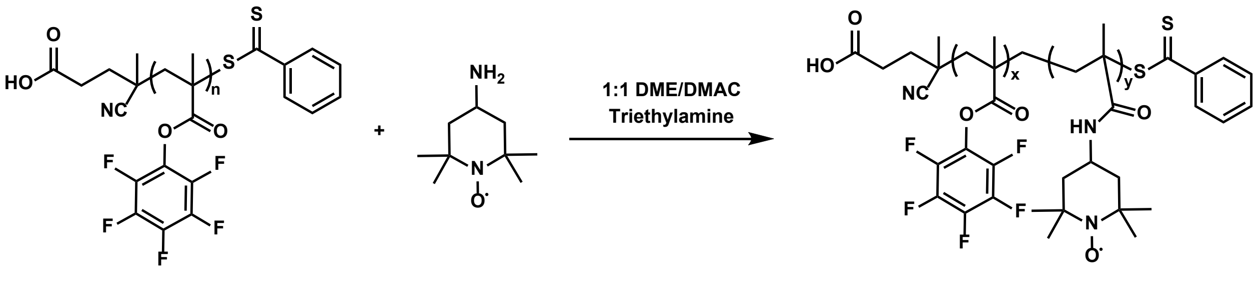
Unless otherwise stated, all reagents and solvents were purchased from Sigma–Aldrich, Alfa Aesar and Combi-Blocks and used as received without further purification. Poly(pentafluoromethacrylate) and poly(TEMPO methylacrylamide) (PTMAM) were prepared according to previously published procedures.[1,2] Brief synthetic procedures used in this work are reported below. Nuclear magnetic resonance spectra were recorded using a Bruker Avance III NMR spectrometer operating at 600 MHz (^1H) or 150 MHz (^{13}C) at 300 K. All NMR spectra were calibrated to residual solvent signals. Infrared spectra were recorded using an attenuated total reflectance PerkinElmer Spectrum 100 FT-IR with a diamond stage. IR spectra were recorded from 3500 to 650 cm^{-1}.

Poly(Pentafluorophenyl methacrylate) (PPFPMA)



Pentafluorophenyl methacrylate (1.68 g, 6.66 mmol), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB) (10.4 mg, 37.2 μmol) and Eosin Y (0.46 mg of 0.66 μmol) were added to dimethylsulphoxide (0.6 mL). The solution was degassed for 20 minutes, and subsequently exposed to blue light for 1 week. Dichloromethane (~1 mL) was added, and the crude product was precipitated in ice-cold methanol. The product was reprecipitated in dichloromethane/methanol a further 2 times, and collected as a pale-pink solid, yielding a polymer with M_n = 73,412 g/mol and Đ = 1.41 (1.38 g).

Poly(TEMPO methacrylamide) (PTMAM)



Poly(pentafluorophenyl methacrylate) (0.18 g) and 4-amino-TEMPO (0.24 g, 1.4 mmol) and triethylamine (0.14 g, 1.4 mmol) were added to a 1:1 mixture of 1,2-dimethoxyethane and dimethylacetamide (3.6 mL) in a nitrogen atmosphere. Trifluorotoluene (18 μL) was added as an NMR reference standard. The reaction mixture was stirred at 50ºC for 5 hours. The crude product was precipitated in hexanes, and reprecipitated in acetone/hexanes a further 2 times. An orange solid was collected (0.15 g).

FTIR Spectroscopy (semi-quantitative)

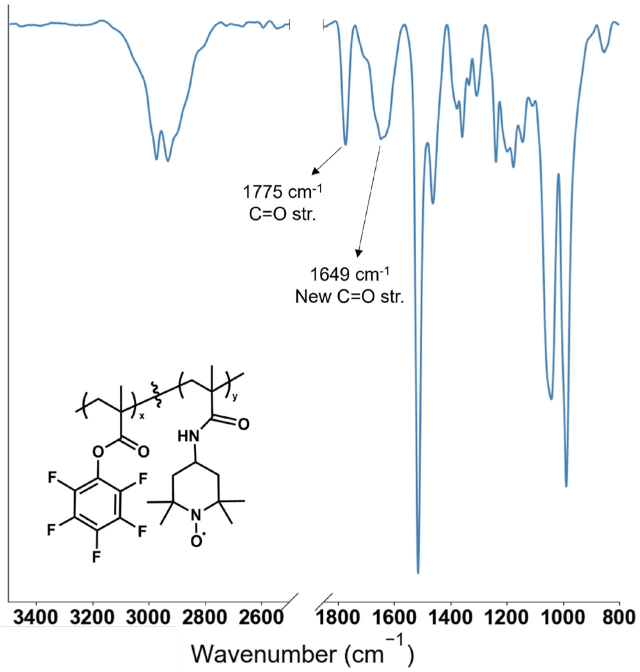


Figure S1. The FTIR spectrum of the synthesised nitroxide ORP. The stretches from the newly formed bonds, amide carbonyl stretch at 1649 cm^{-1}, and the ester stretch at 1775 cm^{-1} are highlighted.

The concentration of 4-amino TEMPO attached during PPM can be found[2] using:

$$\text{percentage conversion} = \frac{I_{am}}{I_{et}+I_{am}+I_{ac}} \times 100$$

where I_{am} corresponds to the intensity of the amide C=O stretch, I_{et} corresponds to the intensity of the existing ester C=O stretch, and I_{ac} corresponds to the intensity of the acid C=O caused by hydrolysis, if present. In our case no hydrolysis was observed, so $I_{ac} = 0$. Given $I_{am} = 4.90$ and $I_{et} = 5.25$:

$$\text{percentage conversion} = \frac{4.90}{5.25 + 4.90 + 0} \times 100$$

$$\text{percentage conversion} = 48$$

The Evans Method

Poly(TEMPO methylacrylamide) (9.4 mg) was dissolved in 1.0 mL of acetone and added to a capillary. The capillary was added to an NMR tube containing $CDCl_3$, and the frequency of the acetone peak recorded. As a reference standard, acetone was added to a capillary, which was subsequently added to an NMR tube containing $CDCl_3$, and the frequency of the acetone peak recorded. Measurements were made using a Bruker Avance III spectrometer operating at 600 MHz at 298 K.

Based on the change in frequency of the acetone peak (Figure 7), the percentage of functionalisation of the ORP was determined. Firstly, the change in frequency is calculated.

$$\Delta F = F_{para} - F_{std}$$

$$\Delta F = 1901.18 - 1862.01 = 39.15$$

Using the concentration of the paramagnetic sample ($c = 9.4 \times 10^{-3}$g/mL), spectrometer frequency ($F = 6.00 \times 10^{8}$ Hz) and ΔF, the mass susceptibility, χ_{m} (cm^3/g) of the sample is calculated.

$$\chi_g = \frac{3}{4\pi}\left(\frac{\Delta F}{F \times c}\right)$$

$$\chi_g = \frac{3}{4\pi}\left(\frac{39.15}{6.00 \times 10^{8} \times 9.4 \times 10^{-3}}\right) = 1.66 \times 10^{-6}$$

The molar susceptibility, χ_m (cm^3/mol) can then be calculated by multiplying the mass susceptibility by the molar mass of a repeating unit with TEMPO attached ($M_w = 254.37$ g/mol).

$$\chi_m = \chi_g \times M_w$$

$$\chi_m = 1.66 \times 10^{-6} \times 254.37 = 4.21 \times 10^{-4}$$

The molar susceptibility is corrected χ_m^{corr} for diamagnetism using $\chi_D = -\frac{M_w}{2} \times 10^{-6}$ emu/mol. [3]

$$\chi_m^{corr} = \chi_m - \chi_D = \chi + \frac{M_w}{2} \times 10^{-6}$$

$$\chi_m^{corr} = 4.21 \times 10^{-4} + \frac{254.37}{2} \times 10^{-6} = 5.49 \times 10^{-4}$$

The effective magnetic moment, μ_{eff} in Bohr magneton, (μ_B) at temperature, (K) is given by:

$$\mu_{eff} = \sqrt{8\chi_m^{corr}T}$$

$$\mu_{eff} = \sqrt{8 \times 5.49 \times 10^{-4} \times 298} = 1.14\ \mu_B$$

The number of unpaired electrons per repeating unit (n) can therefore be calculated,[4] and multiplied by 100 to give the percentage of functionalisation of the polymer.

$$n = -1 + \sqrt{\mu_{eff}{}^2 + 1}$$

$$n = -1 + \sqrt{1.14^2 + 1} = 0.5192$$

$$\text{percentage conversion} = n \times 100$$

$$\text{percentage conversion} = 0.5192 \times 100 = 51.92$$

Quantitative NMR

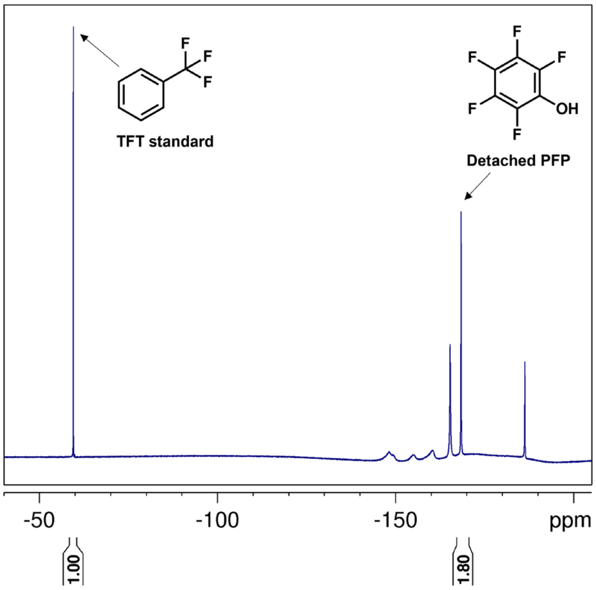


Figure S2. ^{19}F-NMR spectrum of the post-polymerisation modification reaction mixture. A trifluorotoluene (TFT) standard is added. The quantification is based on determining the concentration of detached pentafluorophenol (PFP).

By using quantitative ^{19}F-NMR, the concentration of pentafluorophenol in the reaction mixture can be determined. This directly corresponds to the concentration of radical that has been attached to the polymer, based on the assumption that no hydrolysis is occurring. Based on the concentration of 18 µL of TFT in 3.6 mL of reaction mixture (c_{TFT} = 40.7 mM) the concentration of PFP can be determined using quantitative NMR, using the integrations I_{TFT} = 1.00 and I_{PFP} = 1.80, and the corresponding number of nuclei for the integrated peaks, N_{TFT} = 3 and N_{PFP} = 2.

$$c_{PFP} = \frac{I_{PFP}}{I_{TFT}} \times \frac{N_{TFT}}{N_{PFP}} \times c_{TFT}$$
$$c_{PFP} = \frac{1.80}{1} \times \frac{3}{2} \times 40.7 \times 10^{-3} = 0.101\ M$$

From this value, the number of moles of pentafluorophenol, and therefore N_{PFP} can be determined.

$$N_{PFP} = c_{PFP} \times v_{rm} \times N_A$$
$$N_{PFP} = 0.101 \times 3.6 \times 10^{-6} \times 6.02 \times 10^{23} = 2.38 \times 10^{20}$$

Based on the mass of polymer added, we can find N_{Pol}, and then therefore determine the percentage of conversion.

$$N_{Pol} = \frac{m}{M} \times N_A$$
$$N_{Pol} = \frac{0.1785}{252.14} \times 6.02 \times 10^{23} = 4.26 \times 10^{20}$$
$$\text{percentage conversion} = \frac{N_{PFP}}{N_{Pol}} \times 100$$
$$\text{percentage conversion} = \frac{2.38\times10^{20}}{4.26\times10^{20}} \times 100 = 55.8$$

References

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[2] W. Xue, H. Mutlu, P. Theato, *Eur. Polym. J.* **2020**, *130*, 109660.
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