

Appendix D

SYNTHESIS OF ADDITIONAL PHOTORESPONSIVE MATERIALS: ALKYL-FUNCTIONALIZED AZOBENZENES AND TELECHELIC AZOBENZENE-FUNCTIONALIZED PEG

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D.1 Introduction

Besides the materials studied in Appendix A and Appendix B, additional synthesis of azobenzenes and azobenzene-functionalized PEG was performed. These materials included azobenzenes functionalized with various lengths of alkyl groups and PEG modified at both ends with azobenzene molecules. It was anticipated that the alkyl-groups on the azobenzenes would be useful for tuning the aggregation number of photoresponsive micelles and the photoresponsive wetting on azobenzene-functionalized diblock adlayers. Unfortunately, photoresponsive behavior was observed in neither of these cases, even with azobenzenes lacking an alkyl tail. Since the change in solubility of unmodified azobenzenes was too small to cause a change in aggregation, decreasing solubility further by adding a hydrophobic groups would have be nonsensical. Telechelic azobenzene-functionalized PEG was anticipated to be useful in rheological experiments probing photoresponsive aggregation. Again, since this photoresponsive behavior was not observed with light scattering, rheological measurements were also abandoned.

D.2 Experimental

D-2

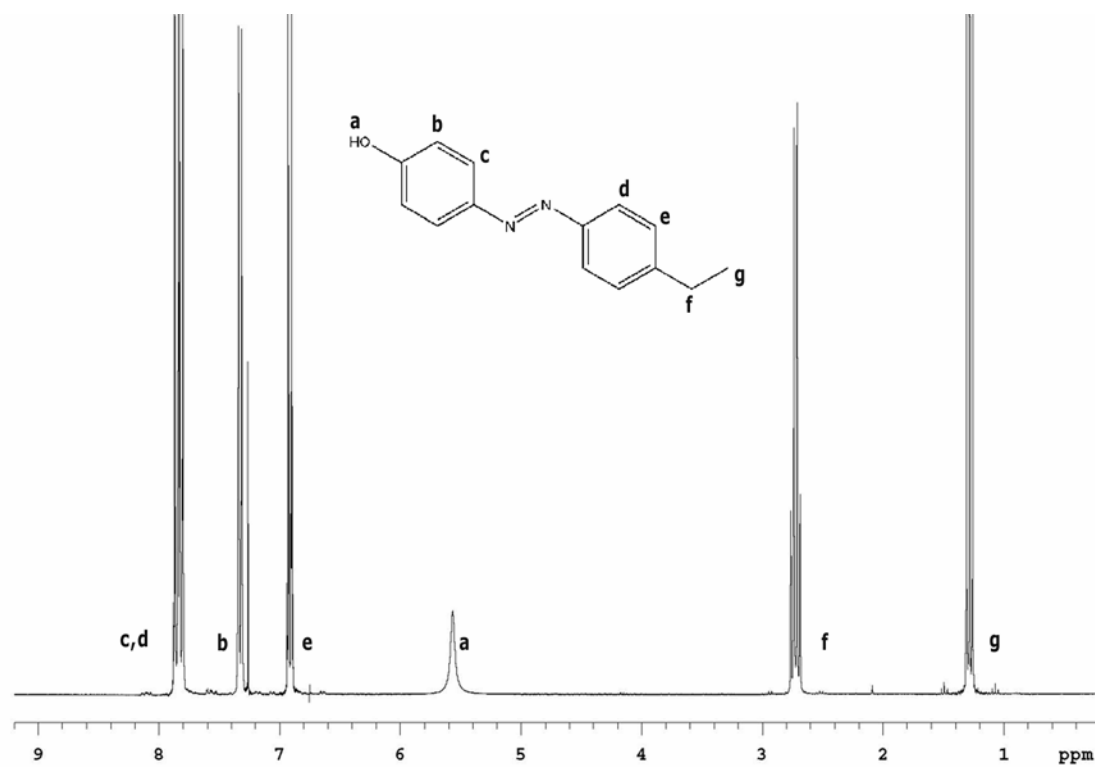
Synthesis of 4-[(4'-Hexylphenyl)azo]phenol (C6-Az-OH), 4-[(4'-Propylphenyl)azo]phenol (C4-Az-OH) and 4-[(4'-Ethylphenyl)azo]phenol (C2-Az-OH) were done in accord with published procedure,¹ noting the misprint of sodium nitrate for sodium nitrite. Except in the case of C2-Az-OH, recrystallization from hexane alone was not sufficient to purify the compound. Silica columns were used to purify C4-Az-OH and C6-Az-OH after an initial recrystallization from hexane. Telechelic azobenzene-functionalized PEG was synthesized in the same manner as PEG modified with azobenzene on only one terminus (Appendix A.)

D.3 Results

Azobenzene Synthesis. The yield of C6-Az-OH was 15.74g (40%), the yield of C4-Az-OH was 12.86g (34%), and the yield of C2-Az-OH was 24.42g (77%). The H¹ NMR matches published results (Figure 1, a-c).

Telechelic Azobenzene-Functionalized PEG Synthesis. NMR showed no unreacted tosylates present, and GPC showed a monomodal distribution (Figure 2, a&b). Percent modification was calculated from the NMR spectra by comparing the integration of the final two hydrogens on the PEG chain ($\delta = 4.2$ ppm) with the integration of the backbone hydrogens ($\delta = 3.65$ ppm). The percent substitution of the Az-PEG3400-Az sample was 78% and the percent substitution of the C2-Az-PEG3400-Az-C2 sample was 80%.

D.4 Figures

**Figure D.1a** NMR spectrum of C2-Az-OH.

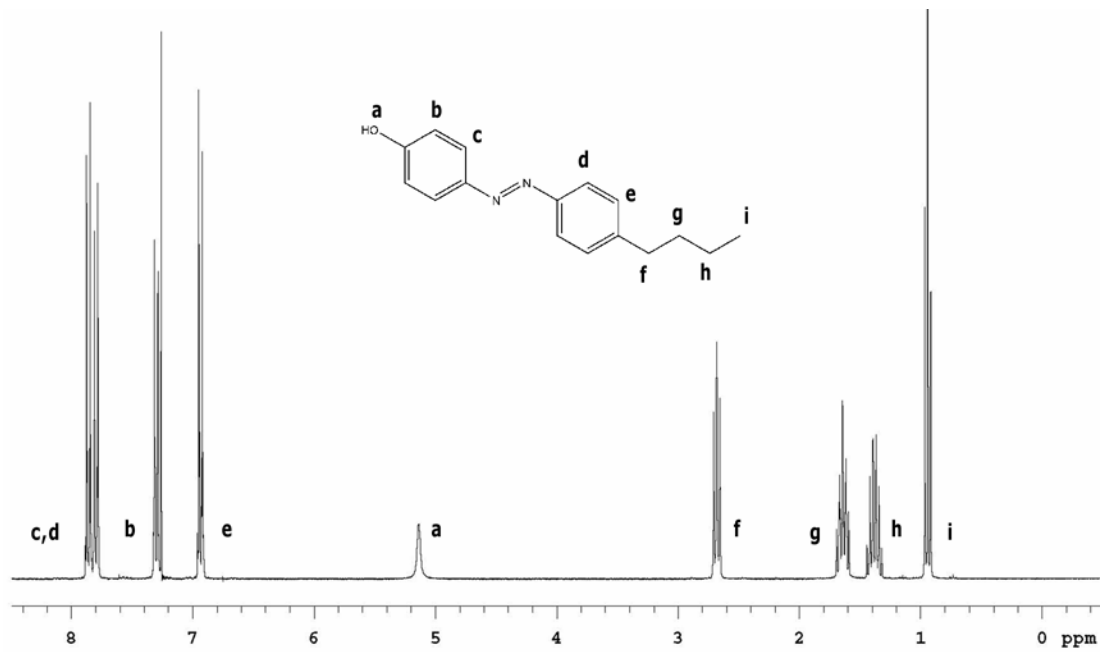


Figure D.1b NMR spectrum of C4-Az-OH.

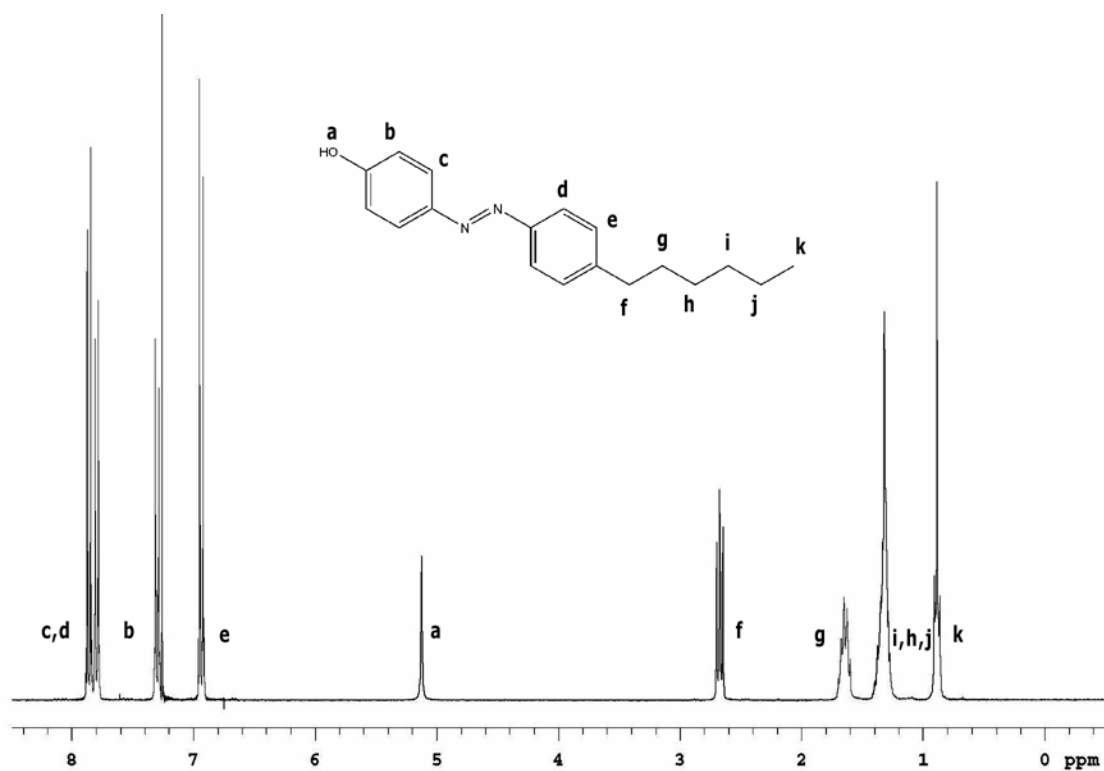


Figure D.1c NMR spectrum of C6-Az-OH.

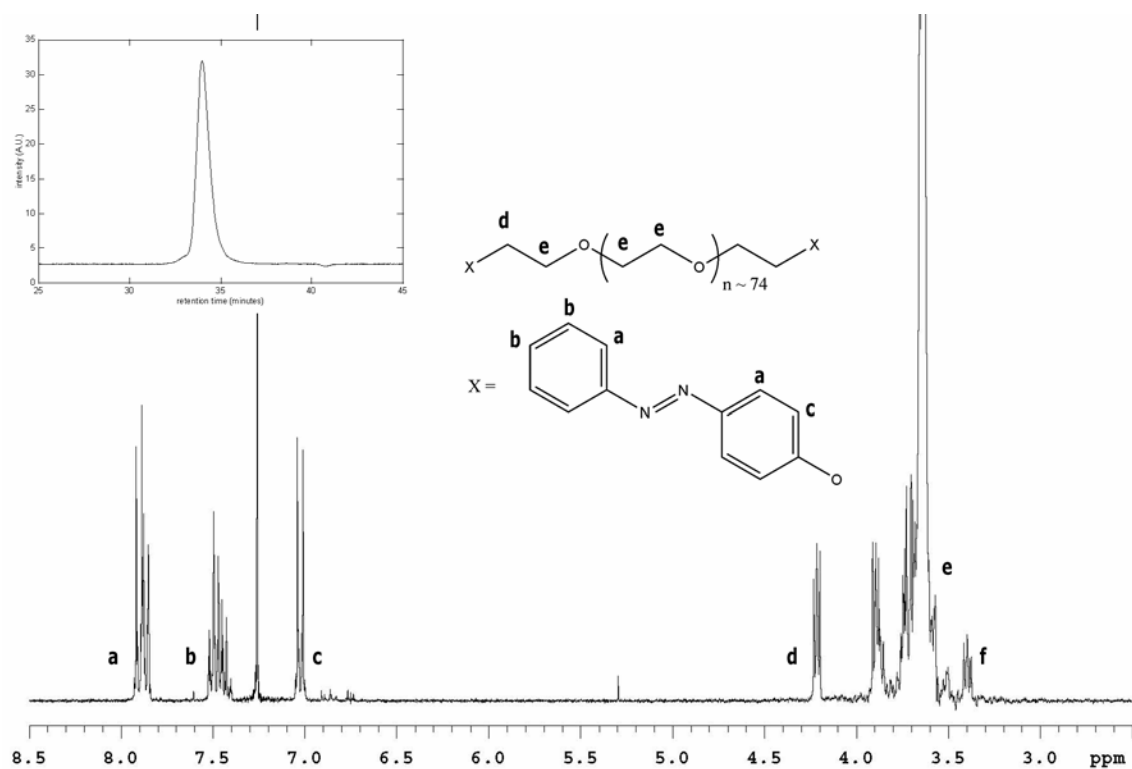
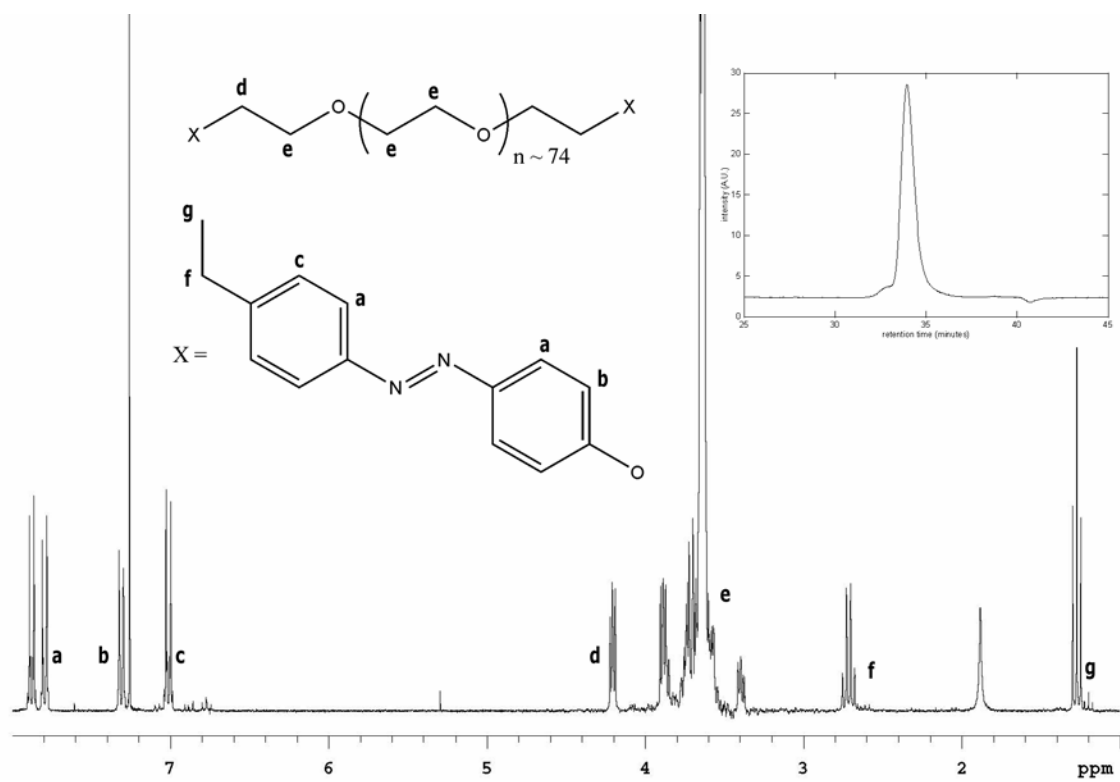


Figure D.2a NMR spectrum and GPC trace of Az-PEG₃₄₀₀-Az.



D.5 References

1. Seki, T.; Sakuragi, M.; Kawanishi, Y.; Suzuki, Y.; Tamaki, T.; Fukuda, R.; Ichimura, K., Command Surfaces of Langmuir-Blodgett-Films - Photoregulations of Liquid-Crystal Alignment by Molecularly Tailored Surface Azobenzene Layers. *Langmuir* **1993**, 9, (1), 211-218.