

It is clearly seen that nitro substituent, [Pn1] and [Pn5], exhibits a low fluorescent intensity. The emission spectra of condensation polymer containing 4-chloro-2,5-diphenyloxazole moiety in polymer backbone studied in THF are shown in Figure 4.15.

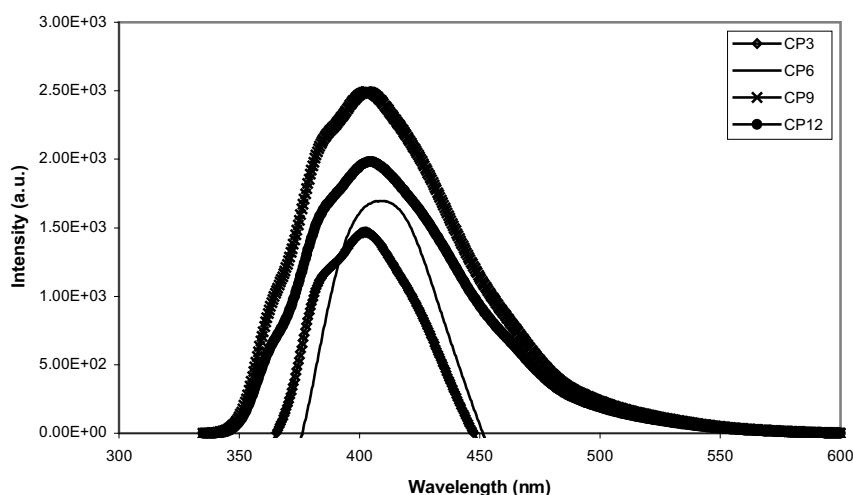


Figure 4.15 Emission spectra of [CP3]-[CP12] at the same concentration

4.6.3 Quantum yield

The highest fluorescent quantum yield is observed for [P1], ($\phi_f = 0.62$). The 1% feed amount of 4-chloro-2,5-diphenyloxazole chromophore gave a higher fluorescent quantum yield than 5%. The high concentration of 4-chloro-2,5-diphenyloxazole moiety probably quench the fluorescence resulting a lower fluorescent quantum yield.

Chapter V

Conclusion

Novel monomers containing 4-chloro-2,5-diphenyloxazole moiety have been successfully synthesized with reasonable yield via a cyclization of the benzoyl cyanide derivatives and corresponding benzaldehyde. These monomers have been tailored for further react with methyl methacrylate and bisphenol A, in order to make a polymer containing 4-chloro-2,5-diphenyloxazole moiety as a pendent chain and in the polymer backbone by free radical and condensation polymerization, respectively.

In term of free radical polymer, acrylate monomers with various substituents including H, F, OCH₃ and NO₂ were copolymerized with methyl methacrylate (MMA) in a different feed ratio, 1% and 5%. These polymers showed a high thermal stability in the range of 247-280°C due to strong dipolar interactions in the solid state between 4-chloro-2,5-diphenyloxazole moiety in the polymer side chains. The glass transition temperature (*T_g*) valued in the range of 114-128°C and only one transition was observed. Thus, these polymer are substantially amorphous in the solid state.

4-Chloro-2,5-bis-(4-fluorophenyl)oxazole monomer was condensed with bisphenol A to make a poly(aryl ether). The optimum polymerization time to obtain a high molecular weight was around 9 h. These poly(aryl ether)s exhibited an excellent thermal stability ranging from 334-364°C and *T_g* valued in the range of 171-205°C.

These two types of polymers containing 4-chloro-2,5-diphenyloxazole have been evaluated the optical properties. All polymer showed the maximum absorption and emission band in the same range as 4-chloro-2,5-diphenyloxazole, parent molecule. Introducing of methoxy and nitro substituents shifted the position of maximum absorption and emission spectrum bathochromically.

The highest fluorescent quantum yield was observed for [P1], $\phi_f=0.62$. The high concentration of 4-chloro-2,5-diphenyloxazole probably quench the fluorescence resulting a lower quantum yield.

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Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

- 1 Pimpha, N., Tantayanon, S., Harris, W. F. (2004) " Synthesis and Characterization of a Novel Poly(aryl ether) Containing 4-Chloro-2,5-diphenyloxazole" Molecular Symposia. (accepted)
- 2 Pimpha, N., Tantayanon, S., Harris, W. F. (2004) " Direct Synthesis of Phenyl Substituted 4-Chloro-2,5-diphenyloxazoles" Heterocycles. (prepared for submission)

2. การนำผลงานวิจัยไปใช้ประโยชน์

- เชิงวิชาการ

โครงการนี้มีส่วนช่วยในการสร้างนักวิจัยใหม่ที่มีความรู้และเชี่ยวชาญด้านการสังเคราะห์พอลิเมอร์และการวิเคราะห์สมบัติทางด้านแสงโดยเฉพาะอย่างยิ่งการนำไปใช้งานด้านซินติเลเตอร์

- เชิงพาณิชย์

โครงการนี้สามารถนำไปประยุกต์ใช้งานได้โดยสามารถแก้ปัญหาที่ 2,5-diphenyloxazole เคลื่อนที่มาจากผิวของพอลิเมอร์และหลุดออก โดยการสังเคราะห์อนุพันธ์ของ 2,5-diphenyloxazole ที่สามารถเกิดพันธะทางเคมีกับพอลิเมอร์ ทำให้อายุการใช้งานของซินติเลเตอร์ที่เป็นพอลิเมอร์นานขึ้น

3. การเสนอผลงานในที่ประชุมทางวิชาการ

1. Pimpha, N., Samingprai, S., Tantayanon, S. " Effect of Substituents on the Formation of 2,5-Diphenyloxazole derivatives" 27th Congress on Science and Technology of Thailand, October 16-18, 2001, Songkla.
2. Pimpha, N., Harris, W. F., Tantayanon, S. " Synthesis and Fluorescence Emission Property of a Novel Fluorescent Polymer" 29th Congress on Science and Technology of Thailand, October 20-22, 2003, Khon Kean.
3. Pimpha, N., Tantayanon, S., Harris, W. F. " Synthesis and Characterization of a Novel Poly(aryl ether) Containing 4-Chloro-2,5-diphenyloxazole" 8th Pacific Polymer Conference, November 24-27, Bangkok.

4. Pimpha, N., Tantayanon, S., Harris, W. F. " Synthesis, Characterization and Optical Properties of Poly(aryl ether) Containing 4-Chloro-2,5-diphenyloxazole Unit" Macro 2004 40th IUPAC world polymer congress, July 4-9, Paris, France.

APPENDIX A

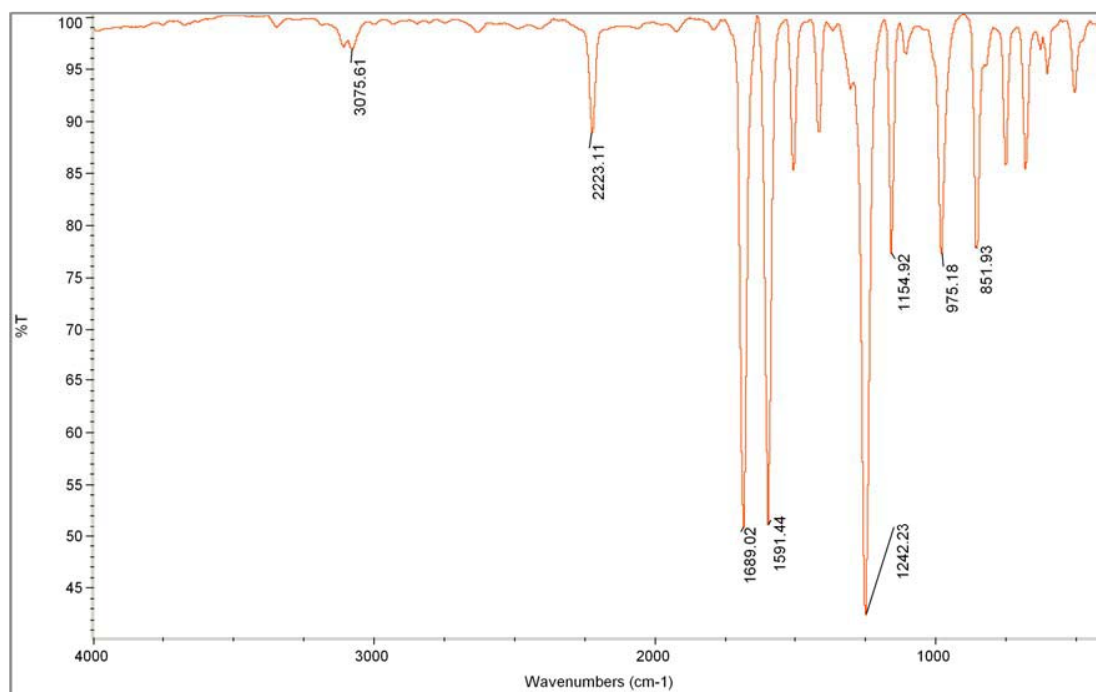


Figure A1 Selected FT-IR spectrum of benzoyl cyanide derivatives

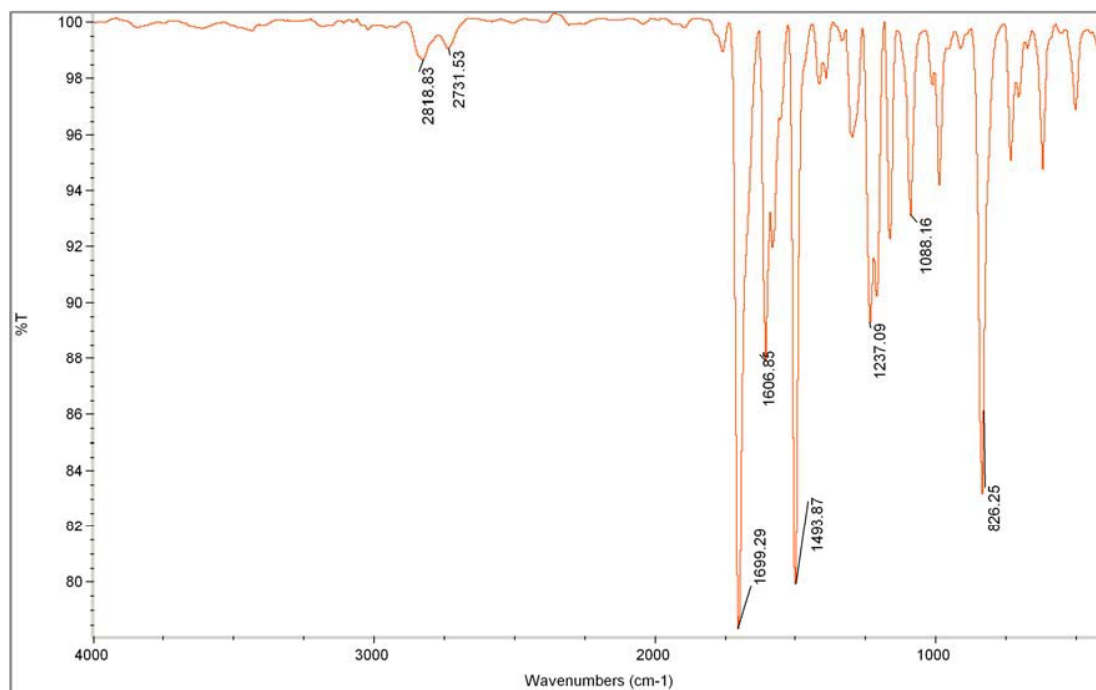


Figure A2 Selected FT-IR spectrum of 4-(4-chloro-5-phenyloxazol-2-yl)-benzaldehyde derivatives

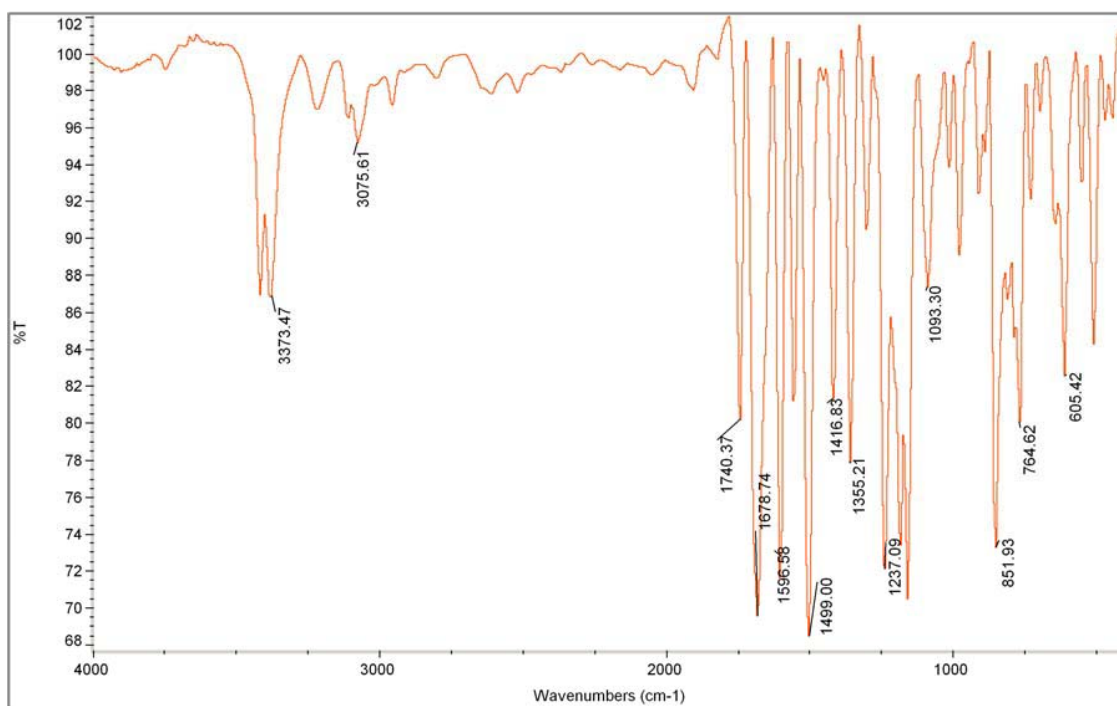


Figure A3 FT-IR spectrum of 4-chloro-2,5-bis(4-fluorophenyl)oxazole

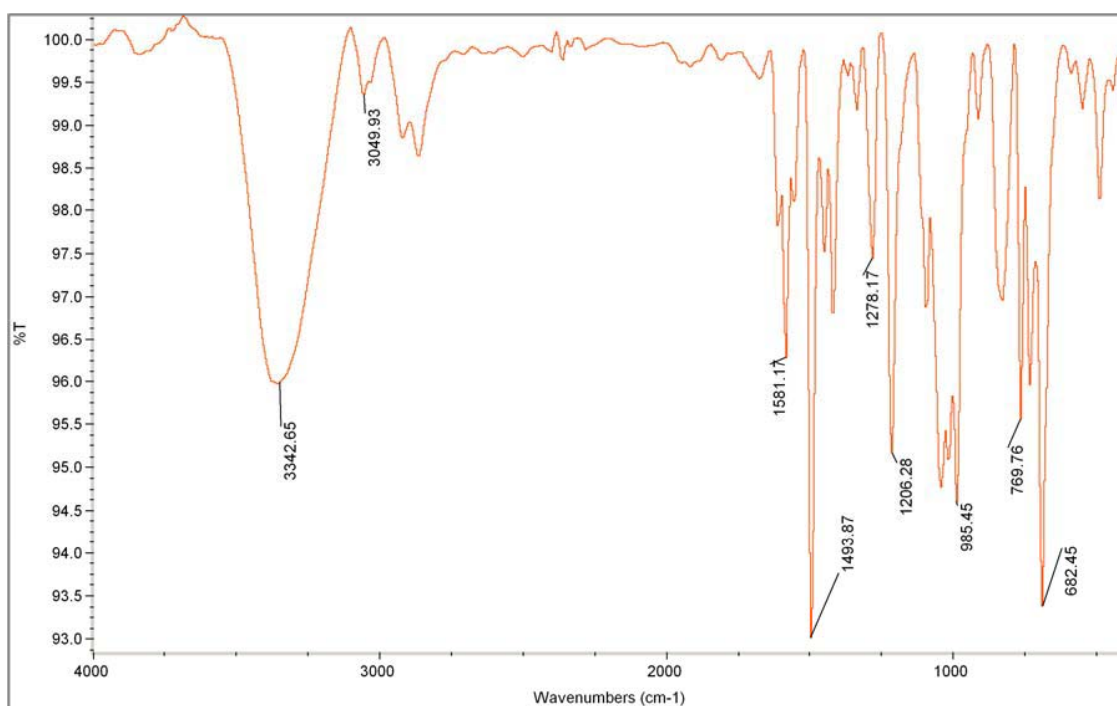


Figure A4 Selected FT-IR spectrum of [4-(4-chloro-5-phenyloxazol-2-yl)-phenyl]-methanol derivatives

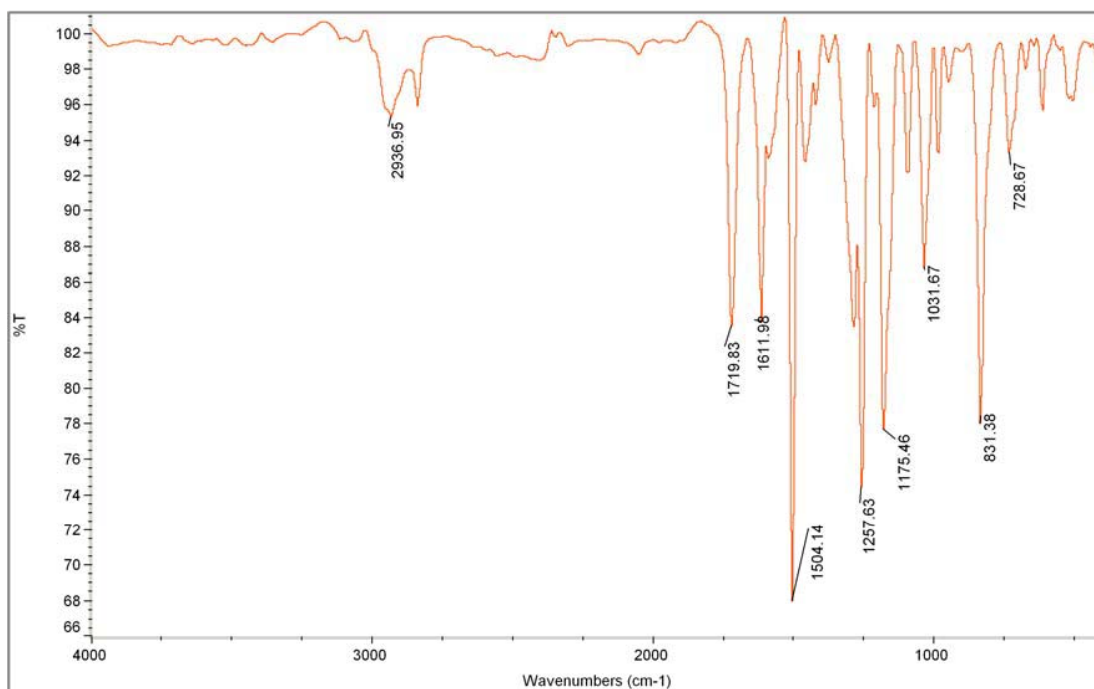


Figure A5 Selected FT-IR spectrum of 2-methylacrylic acid 4-(4-chloro-5-phenyloxazol-2-yl)-benzyl ether derivatives

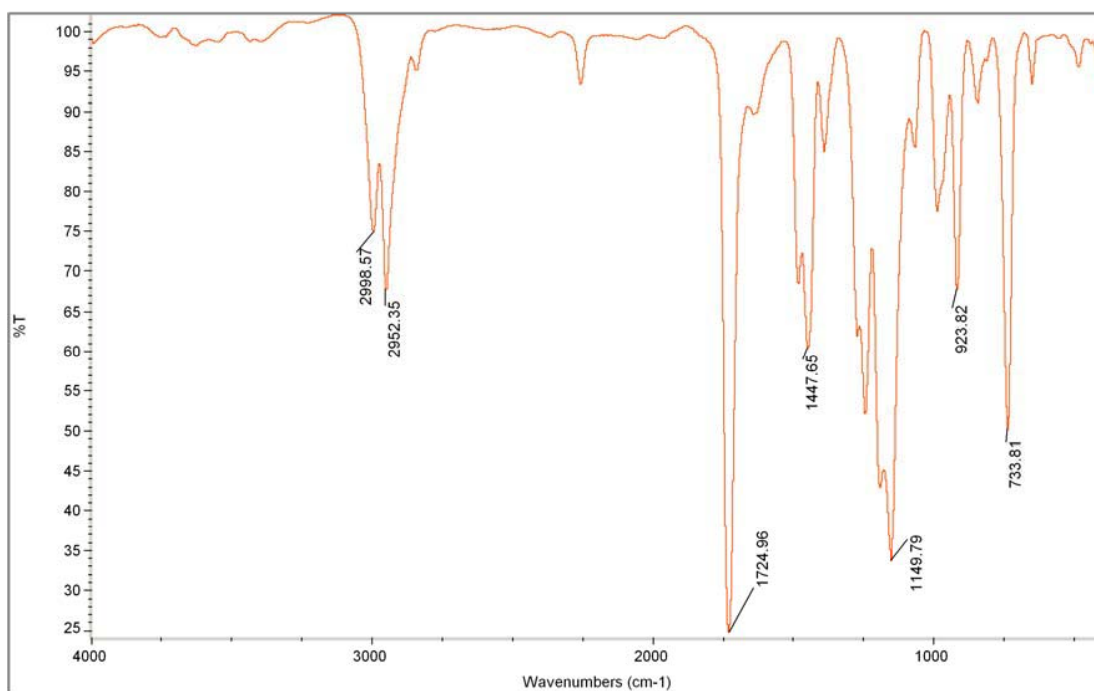


Figure A6 Selected FT-IR spectrum of free radical polymers

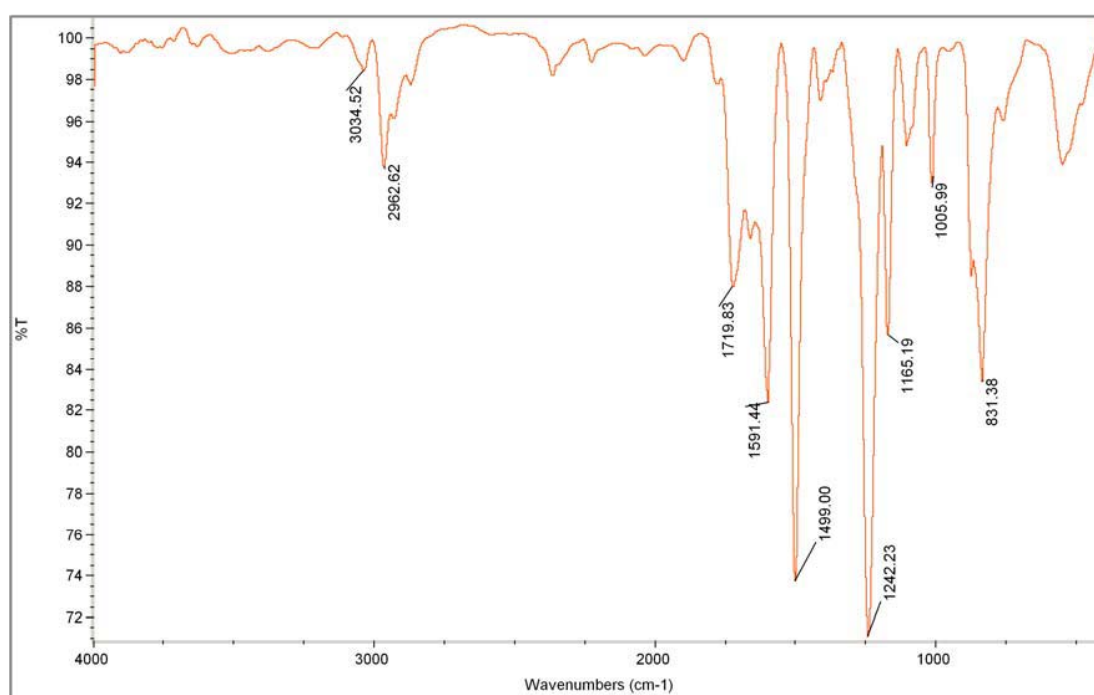


Figure A7 Selected FT-IR spectrum of condensation polymers

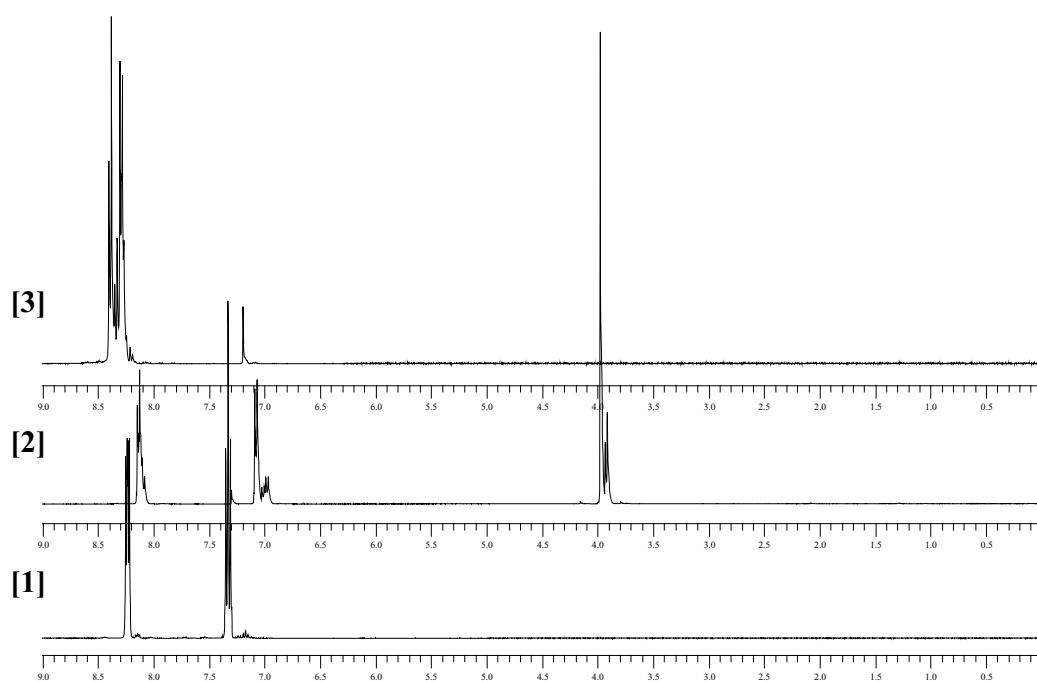


Figure B1: ^1H -NMR of benzoyl cyanide derivatives; fluorobenzoyl cyanide [1], 4-methoxybenzoyl cyanide [2] and 4-nitrobenzoyl cyanide [3]

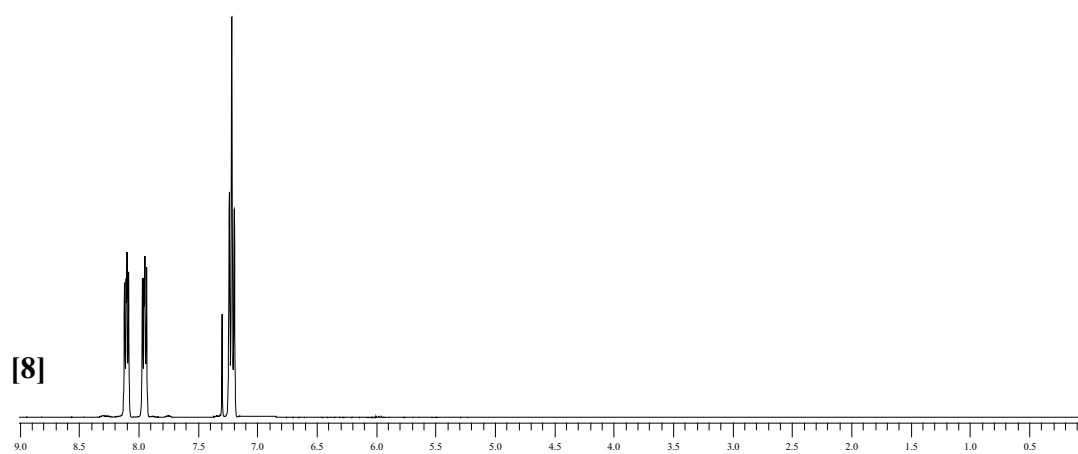


Figure B2: ^1H -NMR of 4-chloro-2,5-bis-(4-fluorophenyl)oxazole [8]

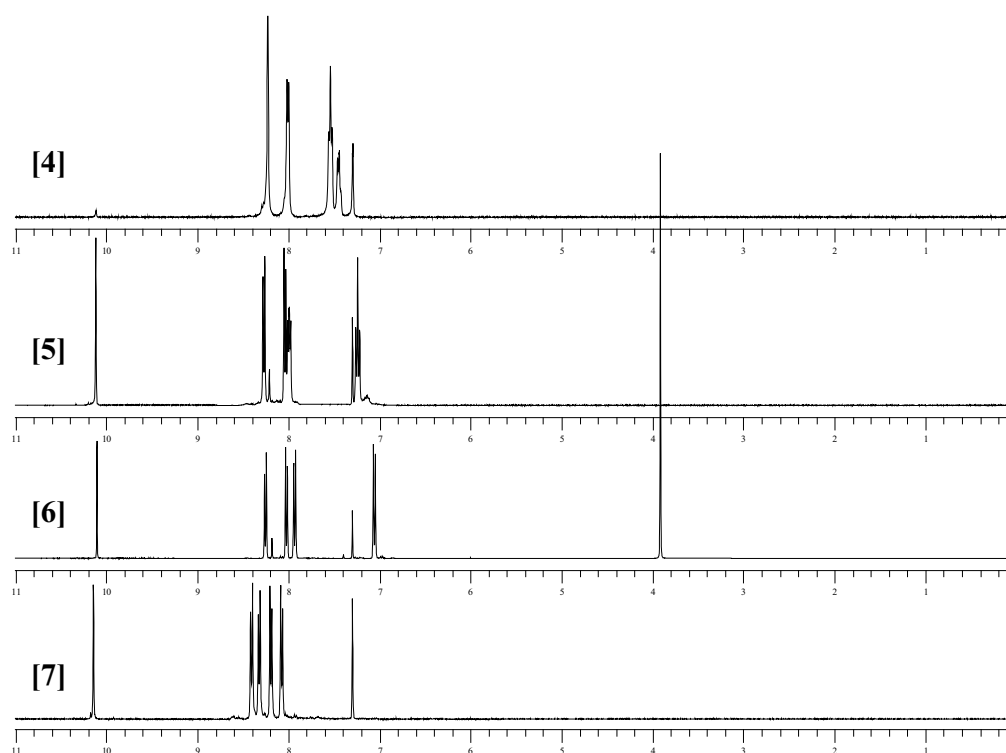


Figure B3: ^1H -NMR of 4-(4-chloro-5-phenyl-oxazol-2-yl)-benzaldehyde derivatives

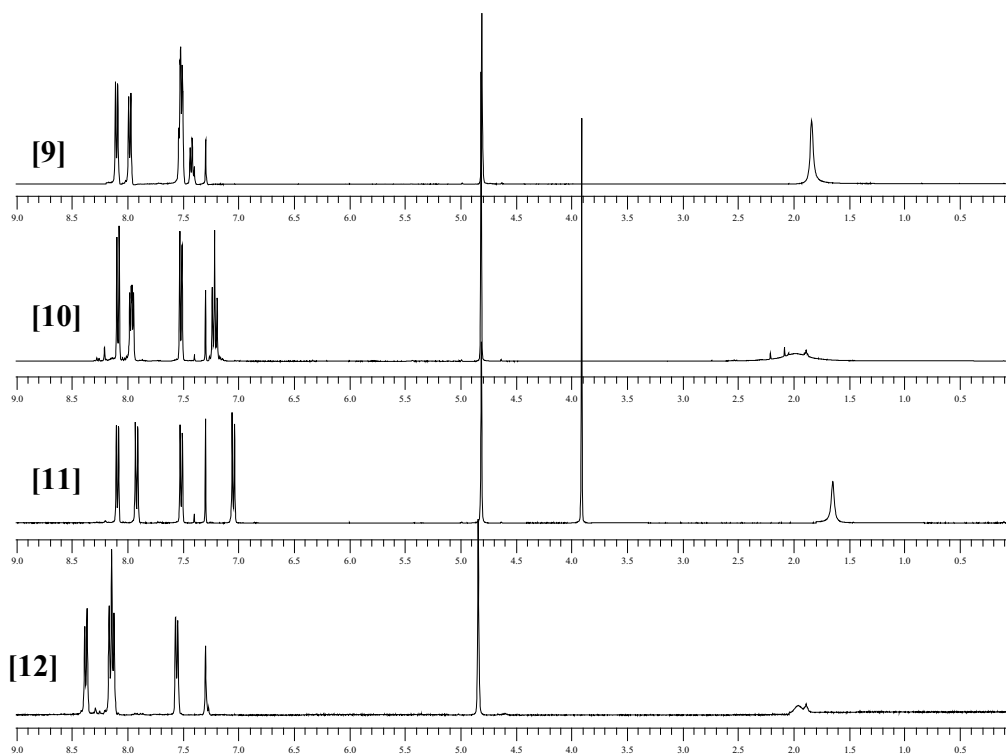


Figure B4: ^1H -NMR of [4-(4-chloro-5-phenyl-oxazol-2-yl)-phenyl]-methanol derivatives

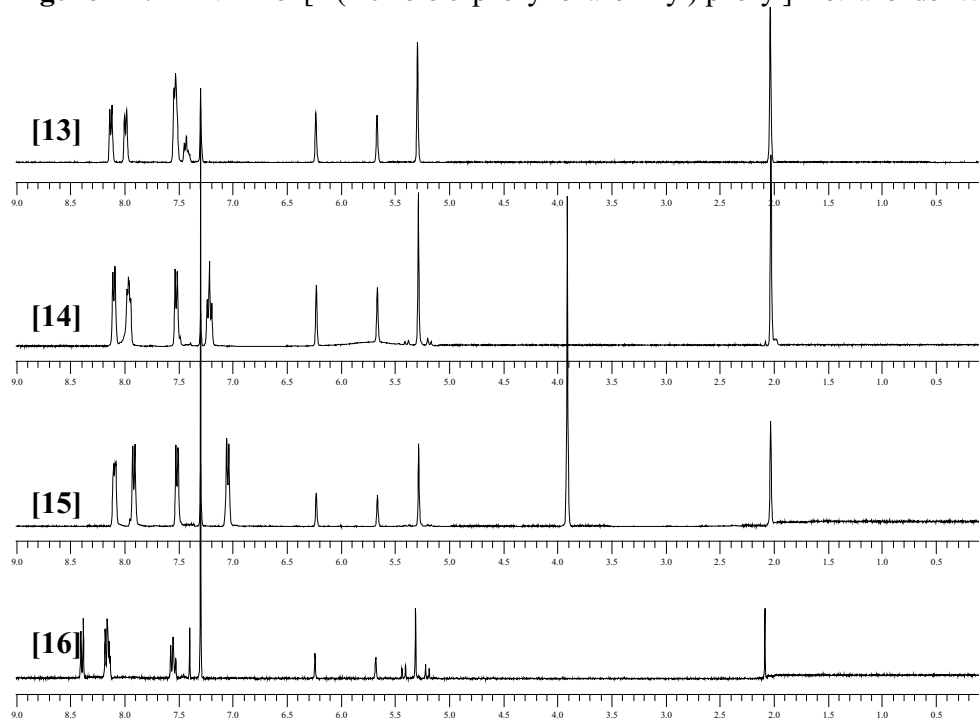


Figure B5: ^1H -NMR of 2-methyl-acrylic acid 4-(4-chloro-5-phenyl-oxazol-2-yl)-benzyl ether derivatives

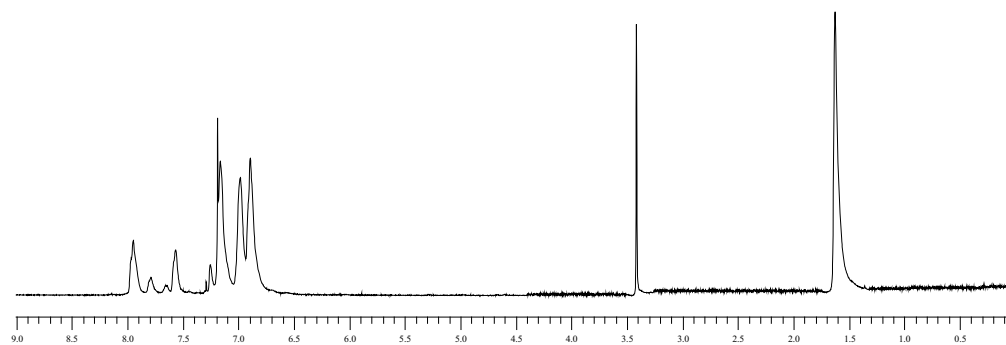


Figure B6: ^1H -NMR of condensation polymer

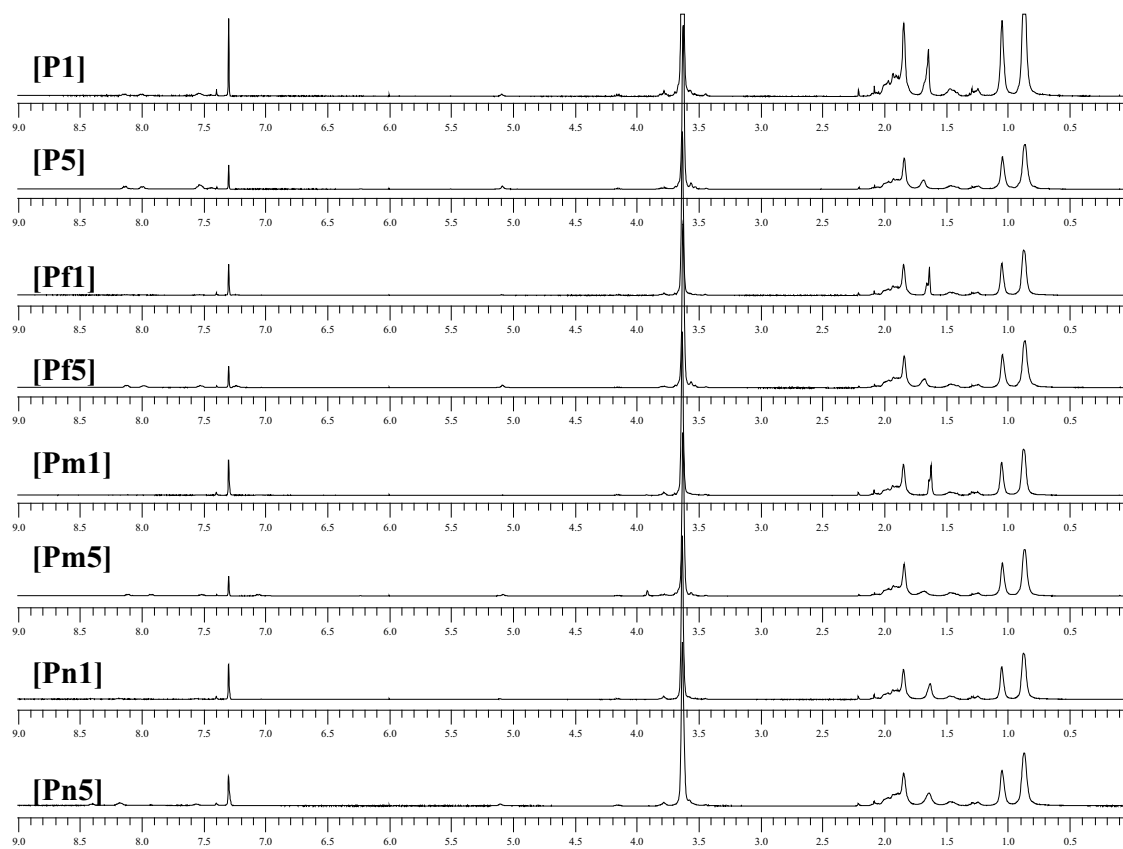


Figure B7: ^1H -NMR of free radical polymers

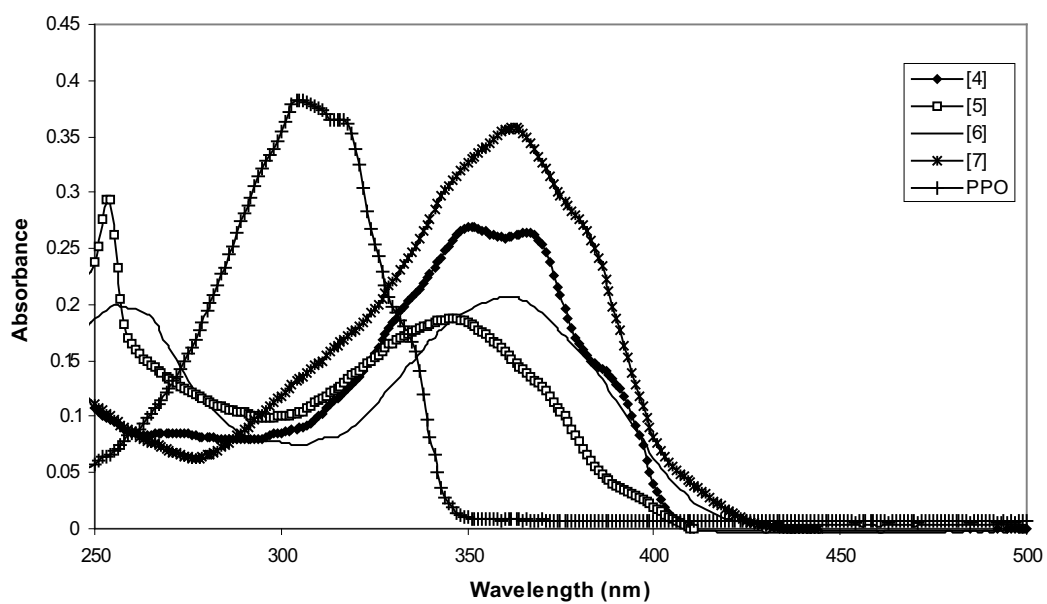


Figure C1: Absorption spectra of compound [4]-[7] and PPO in THF at the same concentration

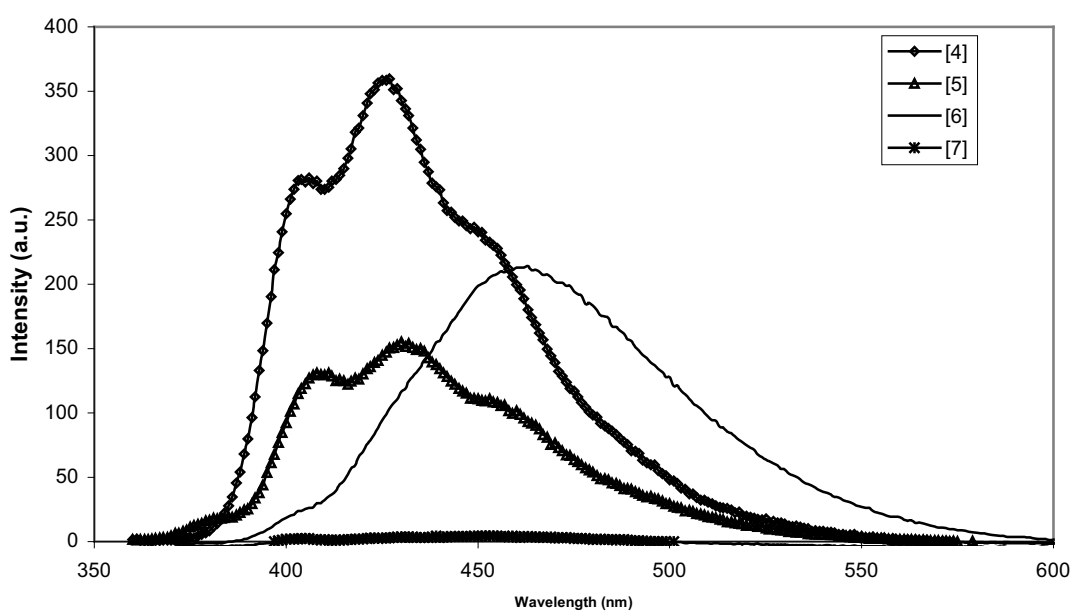


Figure C2: Emission spectra of compound [4]-[7] in THF at the same concentration

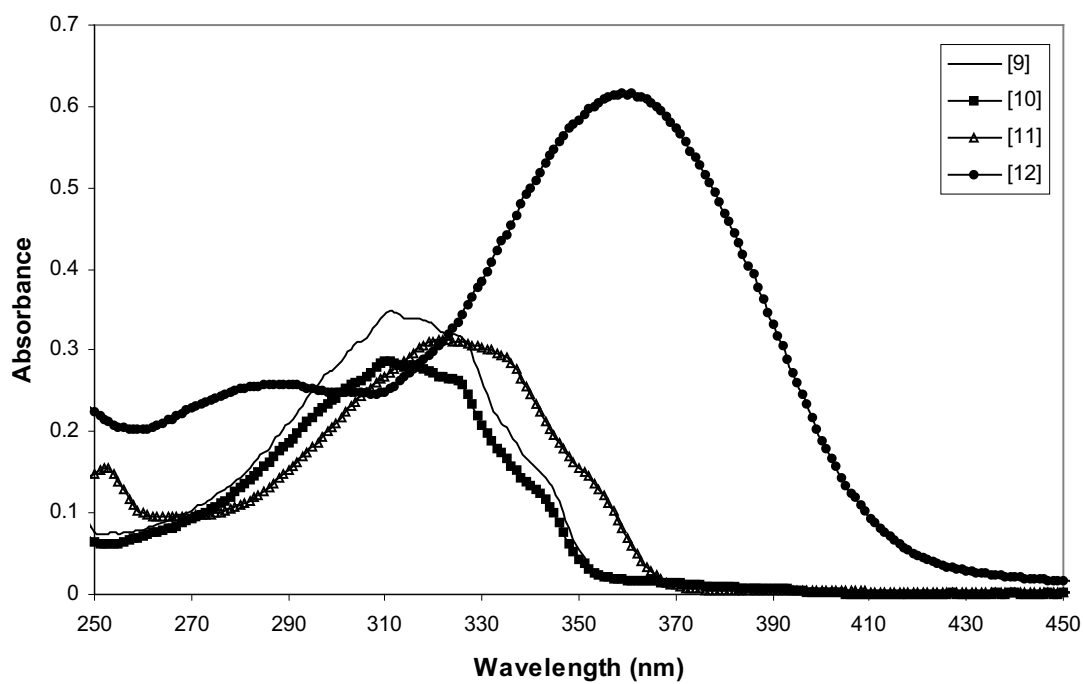


Figure C3: Absorption spectra of compound [9]-[12] in THF at the same concentration

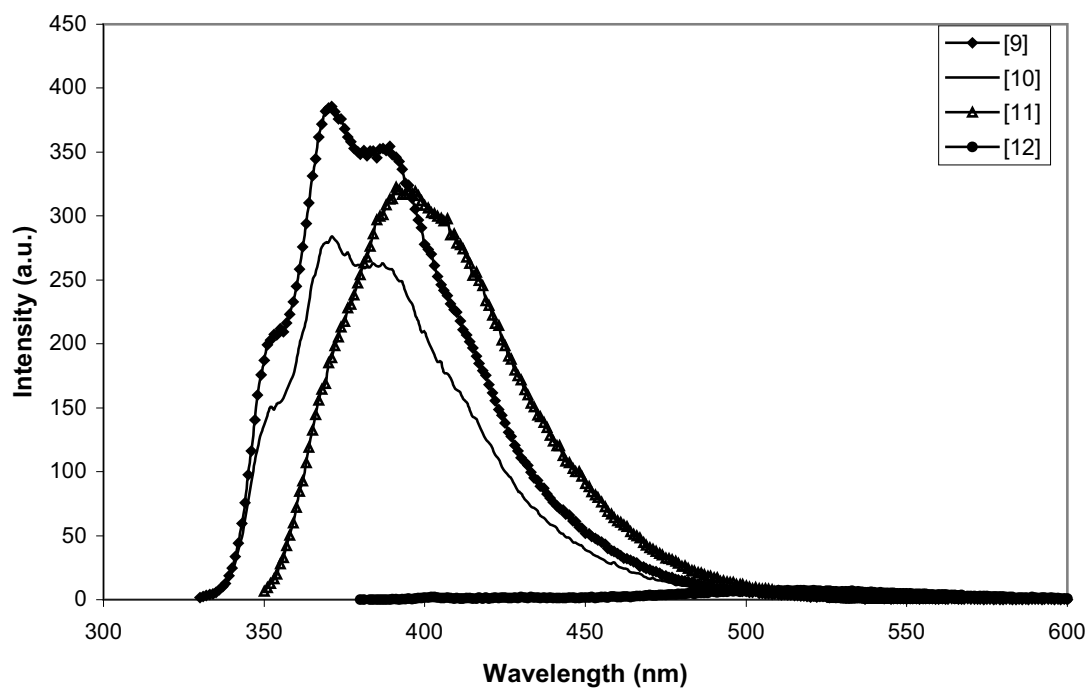


Figure C4: Emission spectra of compound [9]-[12] in THF at the same concentration

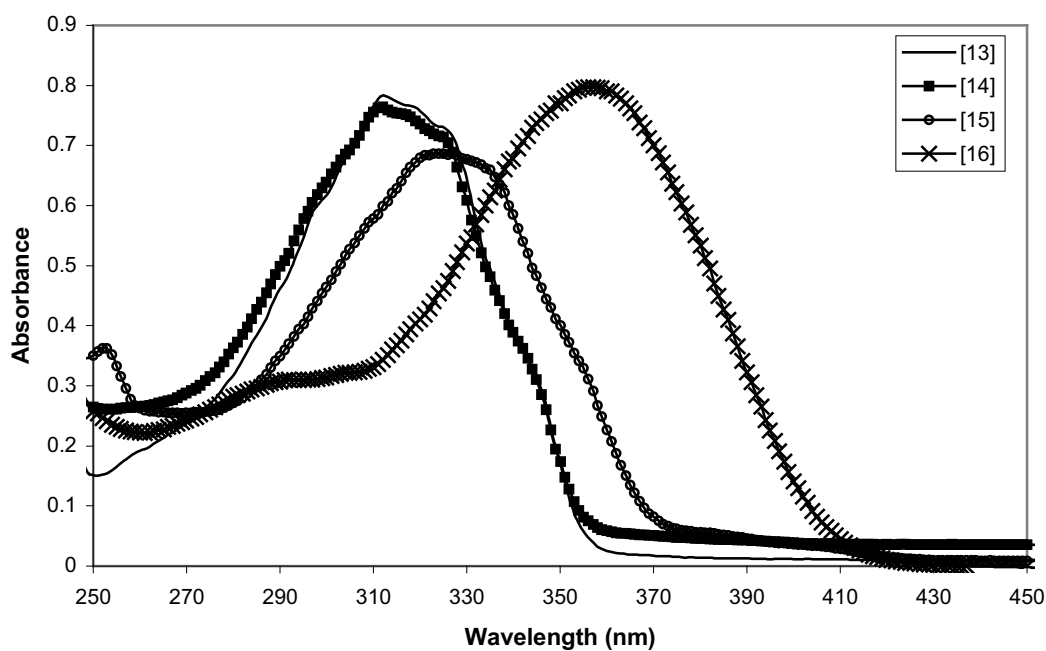


Figure C5: Absorption spectra of compound [13]-[16] in THF at the same concentration

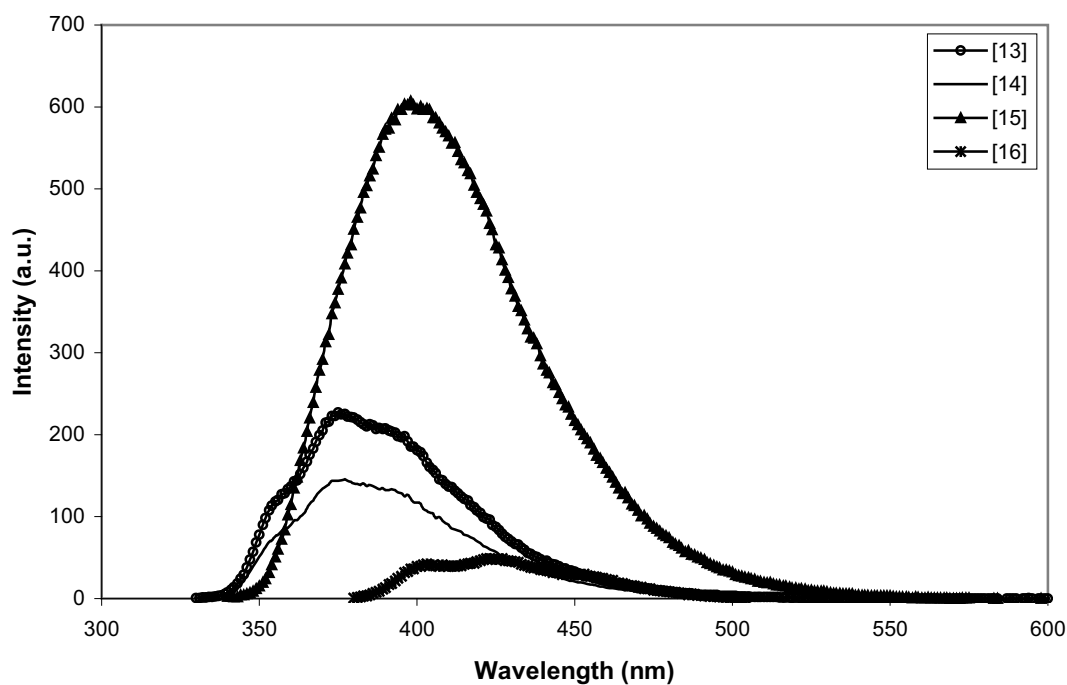


Figure C6: Emission spectra of compound [13]-[16] in THF at the same concentration

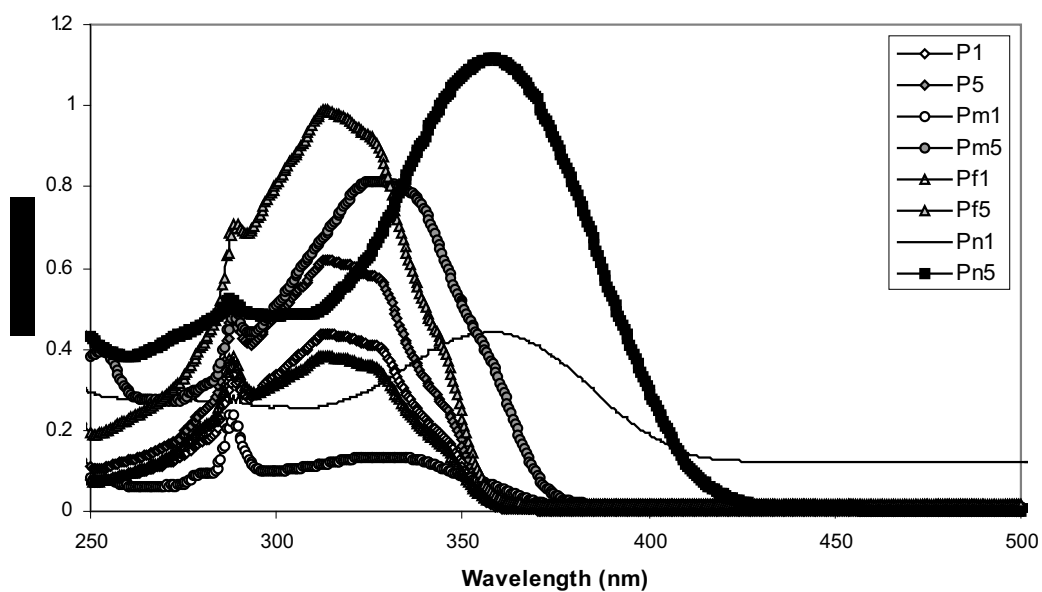


Figure C7: Absorption spectra of [P1]-[Pn5] at the same concentration

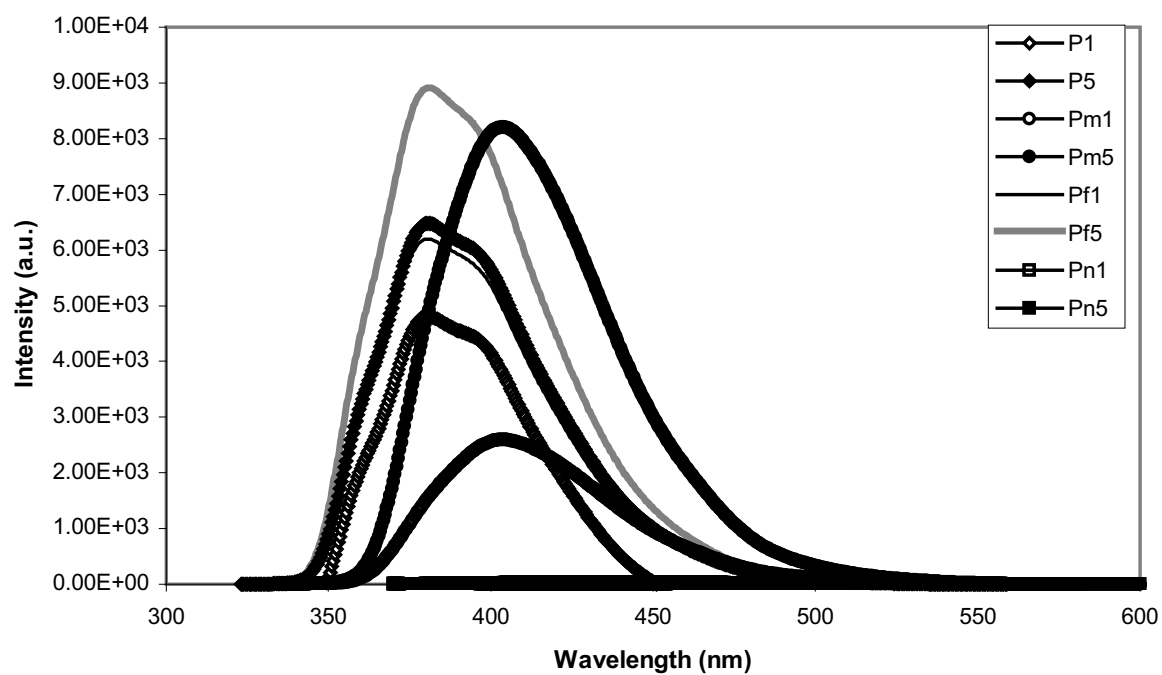


Figure C8: Emission spectra of [P1]-[Pn5] at the same concentration

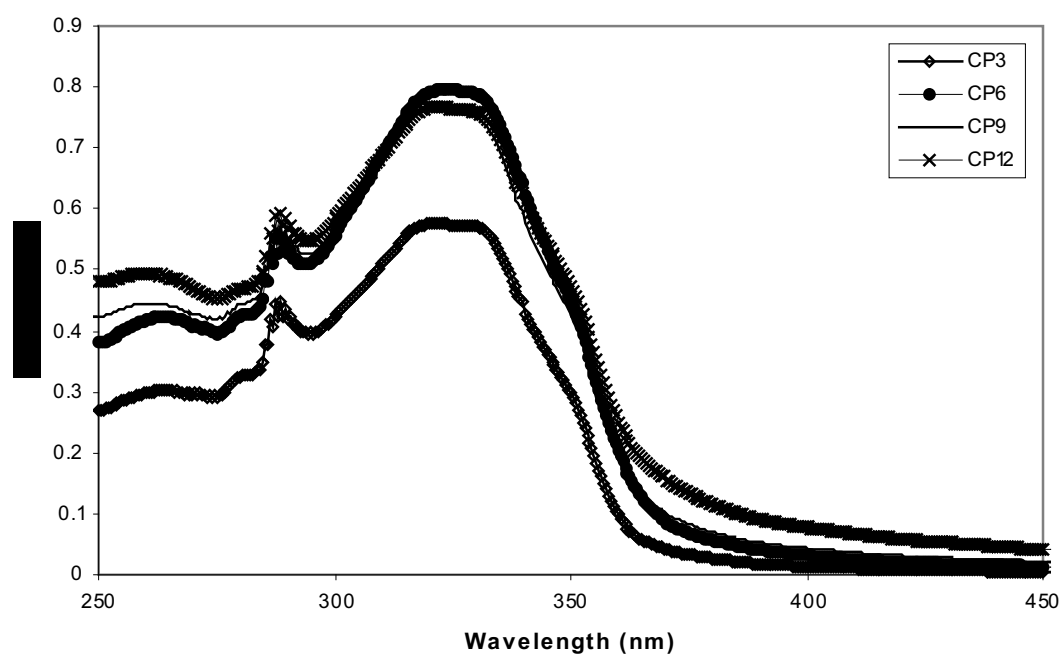


Figure C9: Absorption spectra of [CP3]-[CP12] at the same concentration

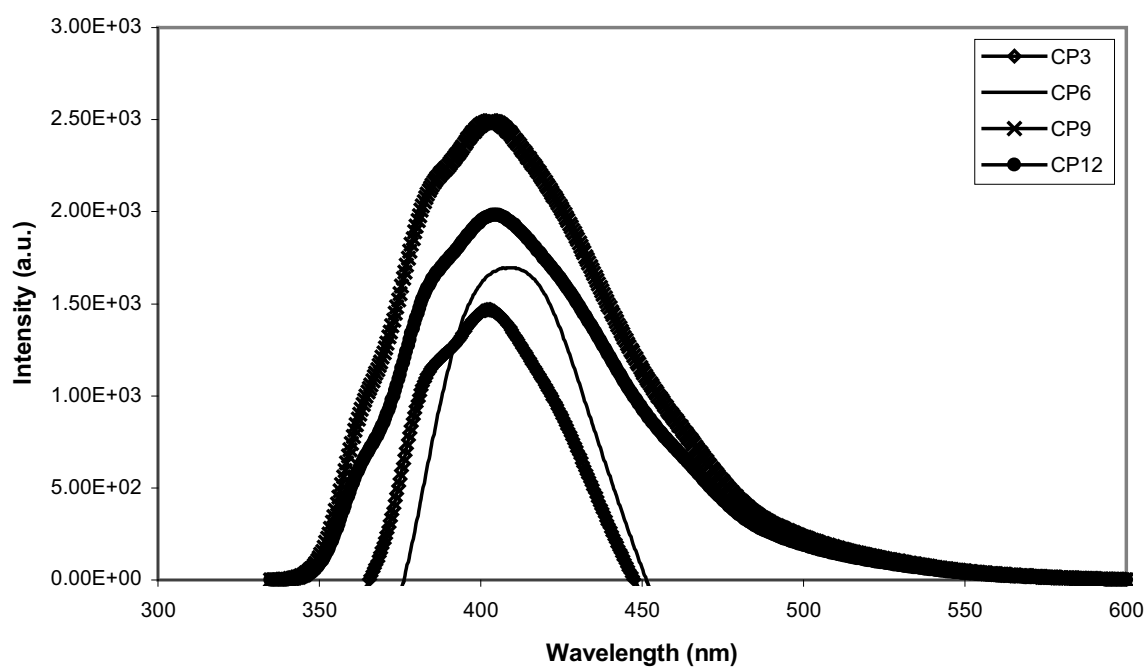


Figure C10: Emission spectra of [CP3]-[CP12] at the same concentration

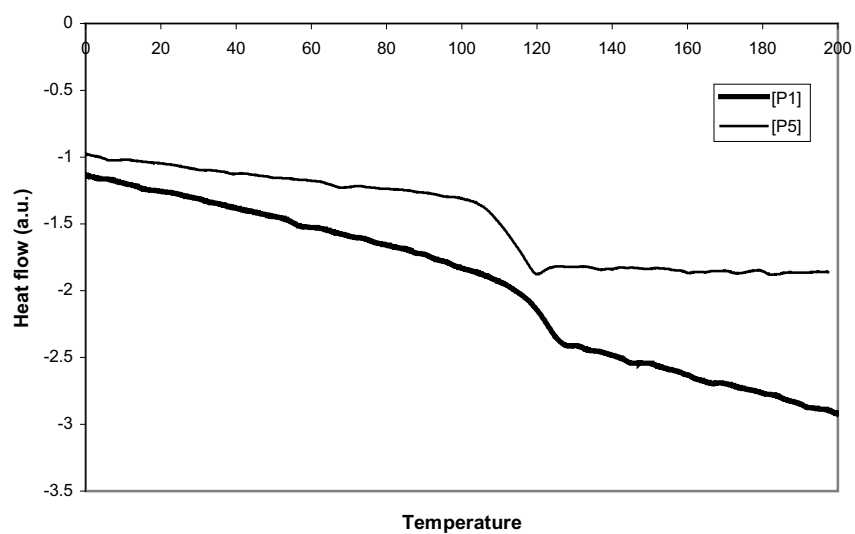


Figure D1: Selected DSC thermogram of free radical polymers

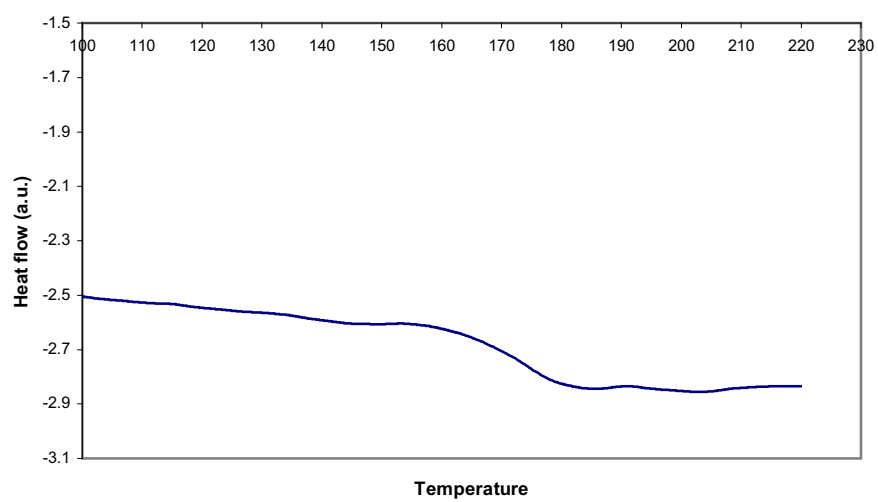


Figure D2: Selected DSC thermogram of condensation polymer