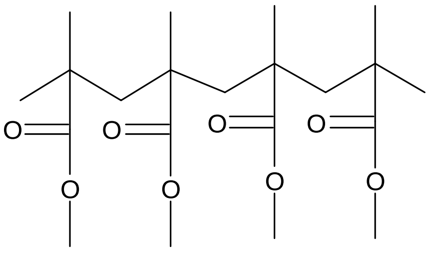
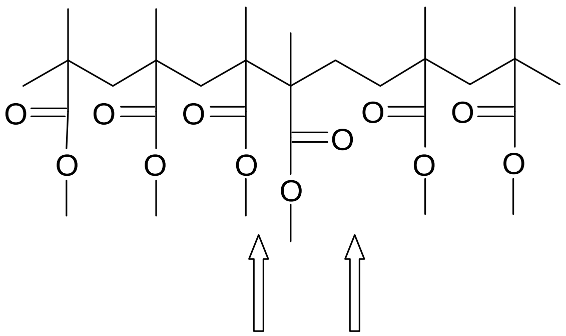
4.3.3 ^{13}C NMR Spectroscopy

The particularly high degradation temperature of the carbazole-phenoxy based methacrylate was a surprising phenomena, particularly in comparison to PMMA. For methacrylate polymerizations, the majority of additions to the polymer chain is a head-to-tail placement, also called a 1,3-placement of monomer units. A small portion of the additions, however, result in a head-to-head placement, also called a 1,2-placement of monomer units. The head-to-tail propagation predominates in chain polymerizations, comprising about 95 % of the repeat unit structure. The small amount of head-to-head linkages typically contribute to the onset of thermal degradation. In effect, the head-to-head linkages, and the subsequent tail-to-tail linkages, are the weak links within the polymer chains, which undergo scission. This scission, which can be cognitively viewed as unzipping, leads to rapid chain degradation.[255]



Head-to-tail linkages



Head-to-head and tail-to-tail linkages

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[255] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 184.

Because the carbazole-phenoxy based methacrylate is so sterically hindered, head-to-head addition should be virtually impossible. The polymer composition of only head-to-tail linkages could explain why the thermal degradation was so high. ^{13}C NMR spectroscopy was used to explore this hypothesis. ^{13}C NMR spectroscopy was also used to investigate tacticity. Noise decoupled ^{13}C NMR spectroscopy was performed on the PMMA prepared in the laboratory, commercial grade PMMA, and the carbazole-phenoxy based methacrylate polymer.

Figure 4.46 shows the ^{13}C NMR spectrum for the lab-scale PMMA; Figure 4.47 shows the spectrum for the commercial grade PMMA. Small, weak peaks from the head-to-head linkages were evident in the methyl carbon peaks between 10 and 25 ppm, particularly in the spectrum for the lab-scale PMMA. The calculations to determine the percent head-to-head linkages are shown below.[256] The lab-scale PMMA had 6.3 % head-to-head linkages. The commercial grade PMMA had 1.1 % head-to-head linkages. Head-to-head linkages are more common when polymerized at higher temperatures,[257] so the commercial grade PMMA was most probably synthesized under milder reaction conditions than the PMMA prepared in the laboratory at 90°C.

Calculation for Head-to-Head Placement of Monomer Units:

$$\frac{\Sigma\ \text{(Integration Values of Head-to-Head Peaks)}}{\Sigma\ [\text{(Integration Values of Head-to-Head Peaks)} + \text{(Integration Values of Head-to-Tail Peaks)}]} \times 100\ \%$$

$$\frac{(0.02 + 0.02 + 0.02)}{(0.02 + 0.02 + 0.02) + (0.03 + 0.36 + 0.50)} \times 100\ \% = 6.3\ \%$$

The large, sharp peak at 51.6 ppm corresponded to the methoxy peak. Tacticity was evident from the carbonyl carbon peaks near 180 ppm, the methylene carbon peaks between 50 and 58 ppm, the quaternary carbon peaks around 45 ppm, and the methyl

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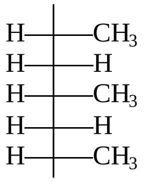
[256] Ohya, T.; Otsu, T., *J. Polym., Sci.: Polym. Chem. Ed.*, **1983**, *21*, 3169.
[257] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 184.

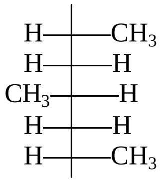
carbon peaks between 10 and 25 ppm. The methyl peaks between 10 and 25 ppm were analyzed for tacticity. The PMMA prepared in the lab contained 4 % isotactic triad tacticity (mm), 40 % heterotactic triad tacticity (mr), and 56 % syndiotactic triad tacticity (rr). This was computed to an overall tacticity of 24 % isotactic configuration (m) and 76 % syndiotactic configuration (r) within the polymer chains for the PMMA prepared in the laboratory. The calculations are shown in Equation 4.6. The commercial grade PMMA contained 2 % isotactic triad tacticity (mm), 35 % heterotactic triad tacticity (mr), and 63 % syndiotactic triad tacticity. This was computed to an overall tacticity of 20 % isotactic configuration (m) and 80 % syndiotactic configuration (r) within the polymer chains for the commercially prepared PMMA. Again, this indicated that the polymerization conditions for the commercially prepared PMMA were milder than for the PMMA prepared in the laboratory. Syndiotactic stereoisomerization is the predominant stereoisometric configuration within polymer chains for these types of polymers. At higher polymerization temperatures, however, more isotactic stereoisomers are present than for polymers produced at lower polymerizations temperatures.[258]

$$\text{Isotactic Percentage} = (m) = mm + \tfrac{1}{2}(mr) \qquad \text{Syndiotactic Percentage} = (r) = rr + \tfrac{1}{2}(mr)$$

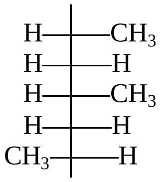
Equation 4.6



Isotactic Triad (mm)



Syndiotactic Triad (rr)



Heterotactic Triad (mr)

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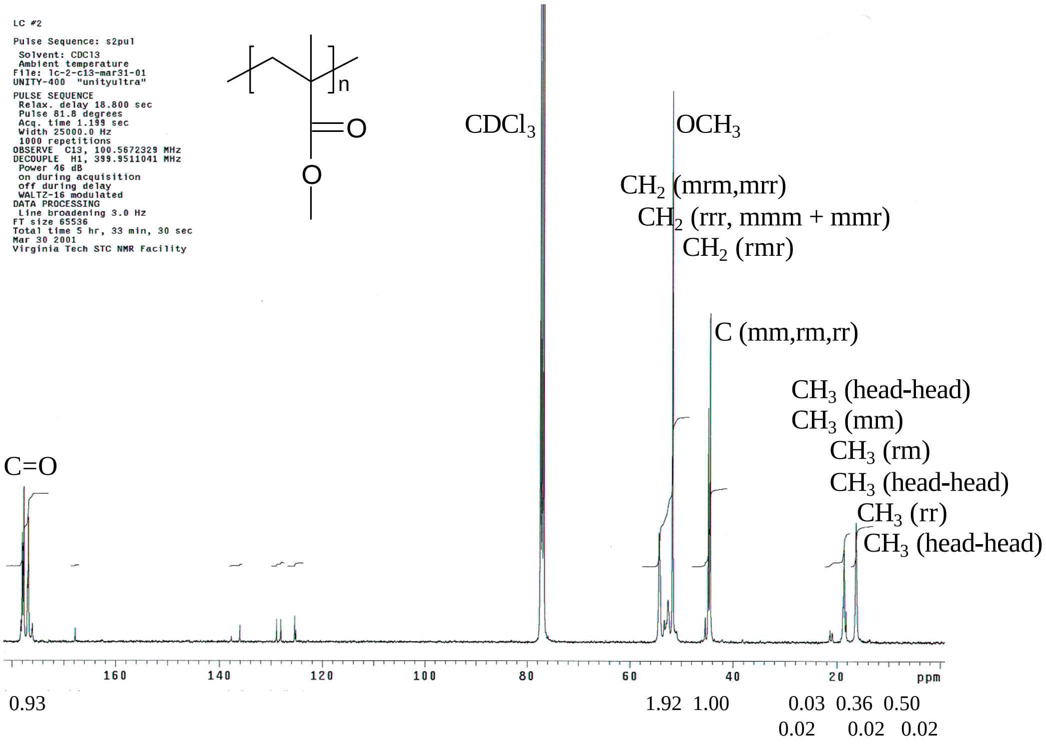
[258] Odian, G., *Principles of Polymerization*, 2nd ed., Wiley: New York, **1981**, 586.



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 Pulse 81.8 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 1000 repetitions
OBSERVE  C13, 100.5672329 MHz
DECOUPLE  H1, 399.9511041 MHz
 Power 46 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 3.0 Hz
FT size 65536
Total time 5 hr, 33 min, 30 sec
Mar 30 2001
Virginia Tech STC NMR Facility
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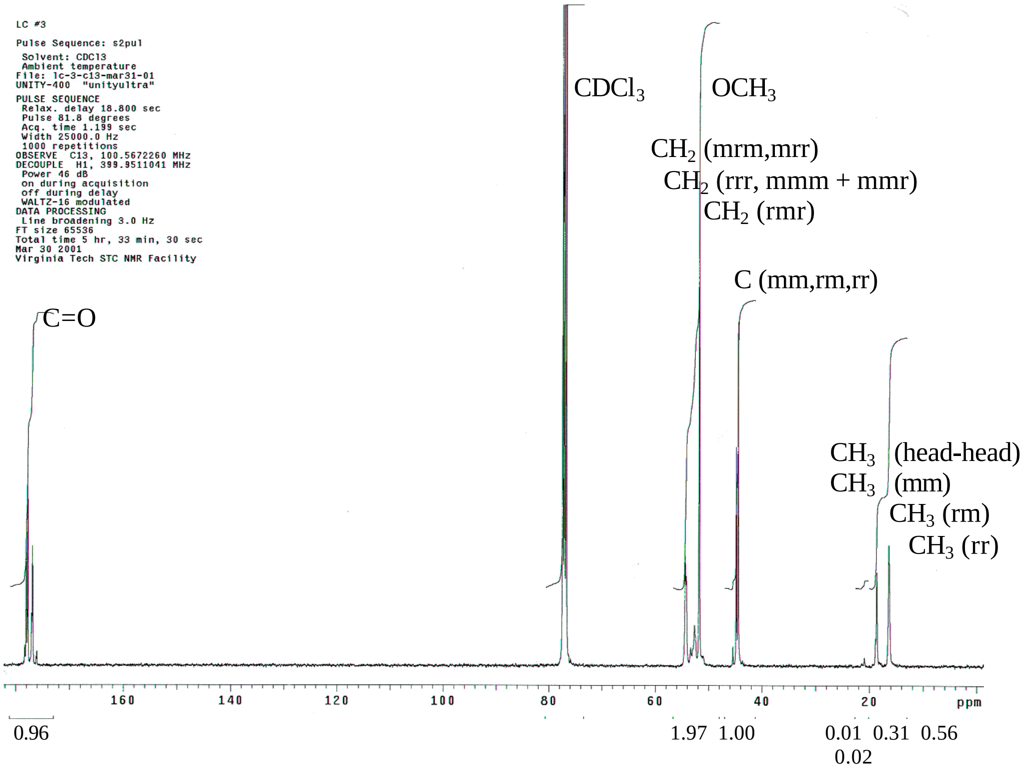
Figure 4.46 ^{13}C NMR Spectrum of Lab-Scale PMMA



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 1000 repetitions
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DECOUPLE  H1, 399.9511041 MHz
 Power 46 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 3.0 Hz
FT size 65536
Total time 5 hr, 33 min, 30 sec
Mar 30 2001
Virginia Tech STC NMR Facility
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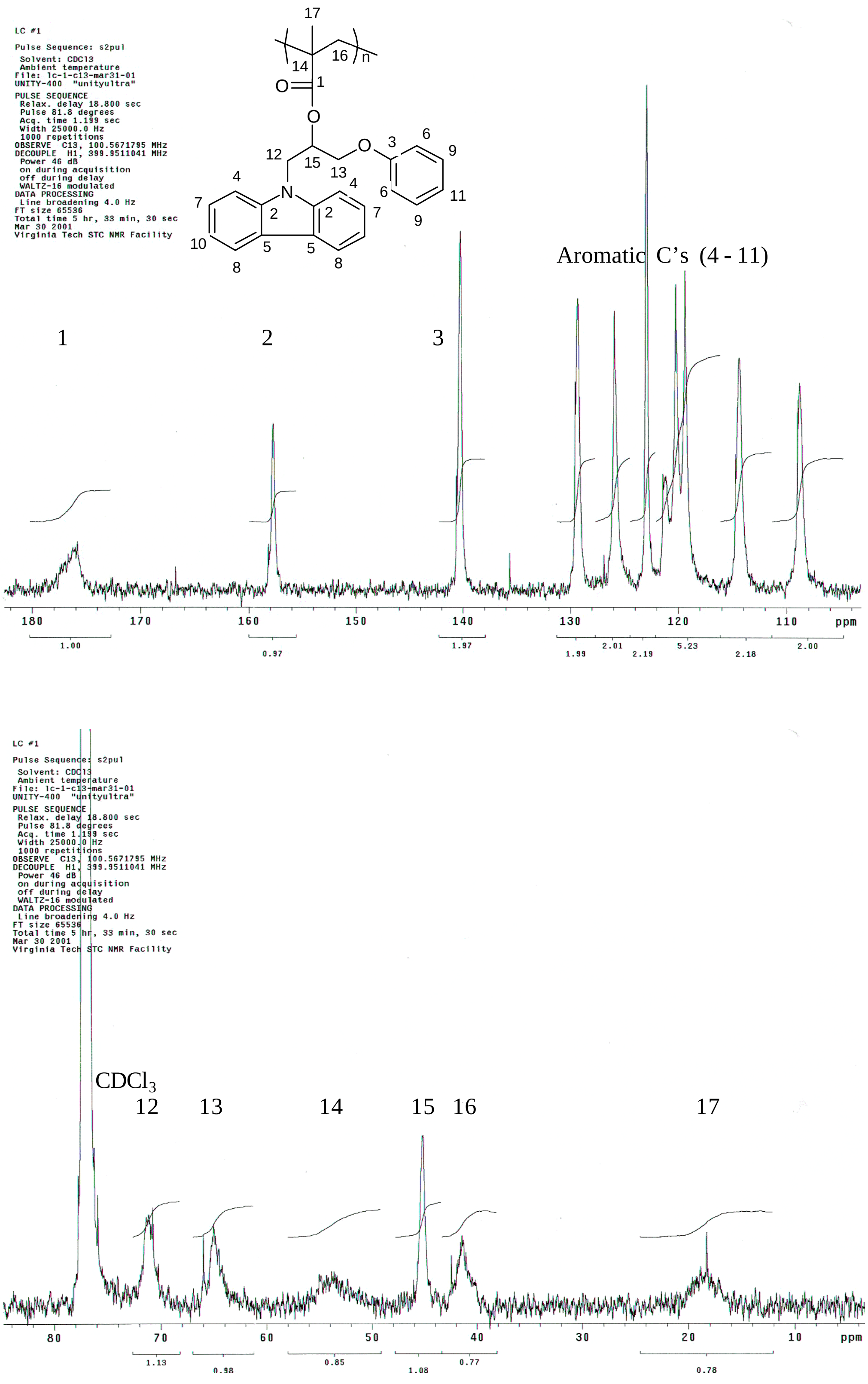
Figure 4.47 ^{13}C NMR Spectrum of Commercial Grade PMMA

Figure 4.48 shows the ^{13}C NMR spectrum for the carbazole-phenoxy based methacrylate homopolymer. Noteworthy was the absence of peaks between 20 and 22 ppm. No peaks could be found for the isotactic triad stereoisomerization (mm) or for the head-to-head placement using this NMR technique. A comparison to the PMMA spectra, using expanded regions, is shown in Figure 4.49. The carbazole-phenoxy based methacrylate polymer did not dissolve well into the deuterated chloroform, so the signal to noise ratio was fairly low, with decreased sensitivity. This experiment was not unequivocal proof, but nonetheless, was evidence that the carbazole-phenoxy based methacrylate contained no detectable isotactic triad configurations or head-to-head linkages within the polymer chains. The absence of head-to-head linkages would provide for a methacrylate with high degradation temperatures, as was the case with the carbazole-phenoxy based methacrylate polymer.

^{13}C NMR analysis of the carbazole-phenoxy based methacrylate polymer did provide additional evidence as to the structure of this highly functionalized polymer. The peak at 176 ppm corresponded to the carbonyl carbon. Ten aromatic carbon peaks between 80 and 160 ppm corresponded to the 10 equivalent carbon atoms from both the carbazole and phenoxy substituents. The peak at 71.5 ppm corresponded to the methylene carbon adjacent to the carbazole group. The peak at 65 ppm corresponded to the methylene carbon adjacent to the phenoxy group. The peak at 53.5 ppm corresponded to the methylene carbon of the methacrylate group. The sharp peak at 45 ppm corresponded to the methine carbon. The peak at 41 ppm corresponded to the quaternary carbon of the methacrylate group. The peak at 18.5 ppm corresponded to the methyl group of the methacrylate group. The methyl peak was very broad, so tacticity was not able to be reliably determined using this analytical method. Because of the large size of the aromatic carbazole and phenoxy substituents, the carbazole-phenoxy based methacrylate polymer was probably configured with a syndiotactic tacticity. Molecular modeling was used to explore the structure of the carbazole-phenoxy based methacrylate polymer further.



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 1000 repetitions
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DECOUPLE  H1, 399.9511041 MHz
 Power 46 dB
 on during acquisition
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Mar 30 2001
Virginia Tech STC NMR Facility
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 Pulse 81.8 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 1000 repetitions
OBSERVE  C13, 100.5671795 MHz
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 on during acquisition
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Virginia Tech STC NMR Facility
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Figure 4.48 ^{13}C of the Carbazole-Phenoxy Based Methacrylate Polymer

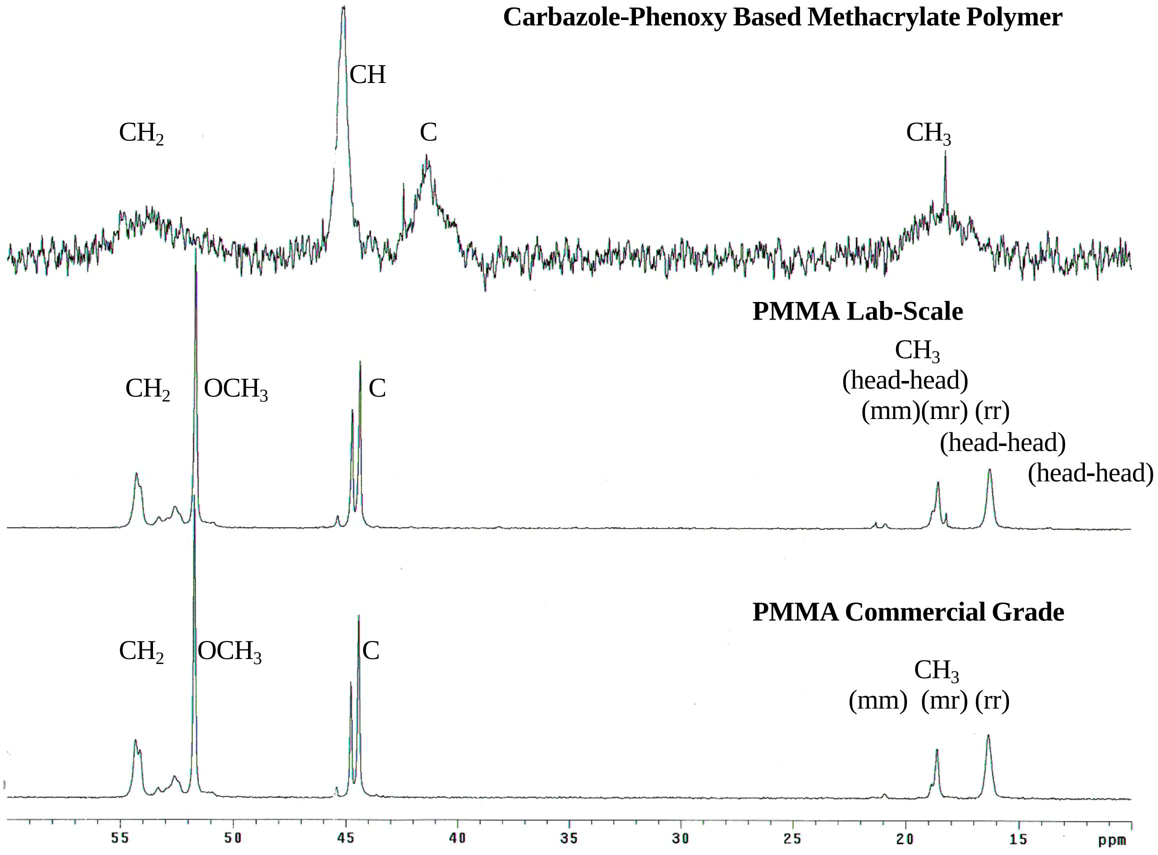

Figure 4.49 Comparison of ^{13}C NMR Spectra, Expanded from 10 to 60 ppm