The ^{13}C and ^{29}Si Nuclear Magnetic Resonance Analysis of Bisphenol A Polycarbonate–Polydimethylsiloxane Block Copolymers

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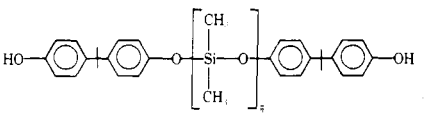
ABSTRACT: A method for complete analysis of bisphenol A polycarbonate–polydimethylsiloxane block copolymers by ^{29}Si and ^{13}C nuclear magnetic resonance spectroscopy is presented. The analysis includes number average block length determinations of both bisphenol A (BPA) polycarbonate and silicone blocks, total polymer composition (percent silicone and BPA polycarbonate), and an analysis of the fraction of isolated BPA units incorporated into the polymer by virtue of the synthetic technique.

Block copolymers of bisphenol A polycarbonate and polydimethylsiloxane, which exhibit a wide range of physical properties depending on their composition and structure, have received considerable academic and commercial interest. The preparation of these polymers is typically carried out in two steps. In the first, an α,ω-dichloropolydimethylsiloxane fluid of relatively low molecular weight is condensed with bisphenol A (BPA) in the presence of an acid acceptor such as pyridine or an alkali metal hydroxide.[1,2] Depending on the molar ratio of the two components, both end-capped fluids (**1**) as well as higher oligomers such as **2** may be formed.



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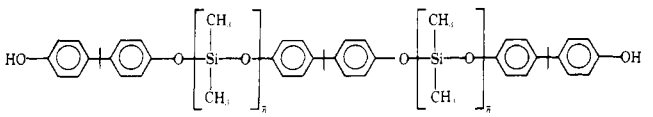

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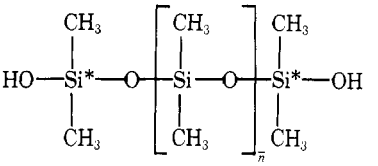
The relative fractions of BPA molecules ending up as terminal oligomer units, as isolated units within oligomers, and as unreacted species may be calculated directly from Flory's equations for copolymerization.[3] The results of such a calculation are expressed graphically in Figure 1 for the case where BPA is the excess component. It is noteworthy that as the molar ratios of the two components approach 1 ($N_{BPA} = N_{PDMS}$) an increasingly greater percentage of isolated BPA molecules are introduced into the oligomers.

In a subsequent step the oligomeric fluid is reacted with additional BPA and phosgene to produce a block copolymer of the desired molecular weight and composition. Since this reaction involves only the hydroxyl moieties, no additional isolated BPA units are introduced into the chains and the average block length is controlled by the relative concentrations of BPA, BPA end-capped dimethylsiloxyl units and their oligomers, and their relative reactivities with phosgene.

As a consequence of this reaction scheme a theoretical estimate of the final average polycarbonate block length and the relative number of isolated BPA units becomes difficult, although both the number of single BPA's and the overall compositional polydispersity is expected to be significantly greater than in copolymers prepared in one synthetic step. For this reason as well as the fact that the physical properties of the silicone–polycarbonate block copolymers are closely linked with composition and sequence length variations, a rapid and convenient analytical technique for determining the average block lengths of the two components as well as the number of isolated BPA units has been needed.

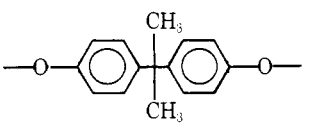
Nuclear magnetic resonance spectroscopy is well established as a valuable technique for determining the microstructure of polymers.[4] In particular, the advent of Fourier transform (FT) NMR has facilitated the observation of low natural abundance nuclei such as ^{29}Si and ^{13}C. Since these nuclei exhibit relatively large chemical shift ranges, resolution of structurally similar atoms by this technique is quite good and FT NMR is particularly well-suited to the analysis of polymer chains where structural changes are small.

Recently we reported the chain length determination of hydroxy terminated dimethylsiloxane oligomers by ^{29}Si NMR.[5] This determination is feasible because the silicon nuclei at the ends of the siloxane chains, Si*, differ in chemical shift by ca. 10 ppm from the internal silicon atoms.



The chain length of the disiloxanol can be calculated directly by integration of the respective peaks. It seemed reasonable to assume that this procedure could be extended to silicone block copolymers as well. To determine the amount of information available by this technique an investigation of the ^{29}Si and ^{13}C NMR spectra of several polydimethylsiloxane–bisphenol A polycarbonate block copolymers (PDMS–BPAP) was recently undertaken. We now wish to report the results of this study: a complete analysis of the polymer composition and microstructure by nuclear magnetic resonance, incorporating the use of both ^{13}C and ^{29}Si spectra in the analysis.

For the purpose of this discussion the XD terminology will be used to refer to the polymers. A D unit refers to one silicone unit (Me_2SiO), and an X unit is a single unit in the BPA polycarbonate block (**5**). The X terminology will also be used to refer to isolated BPA units (**4**) incorporated into the silicone chain.



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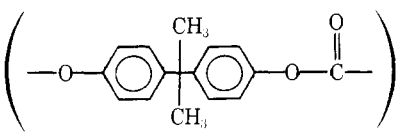

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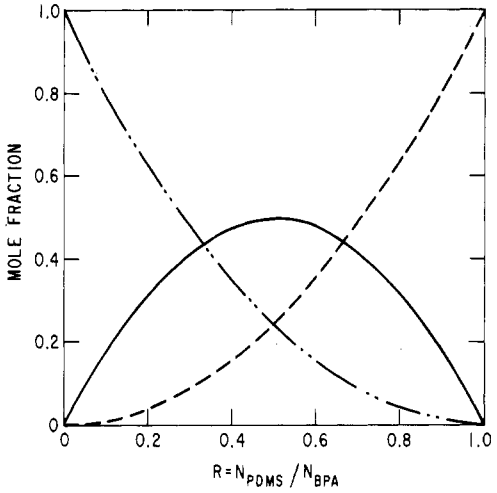
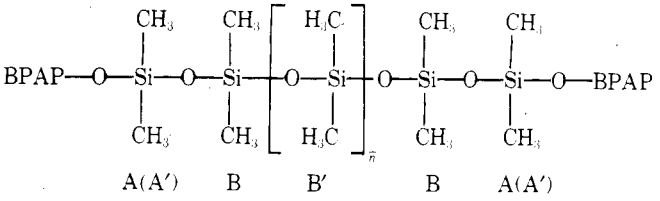


Figure 1. Relative fractions of various BPA species as a function of the initial PDMS and BPA concentrations in the reaction mixture; (- - -) mole fraction of isolated BPA units; (– – –) mole fraction of unreacted BPA molecules; (—) mole fraction of terminal BPA units.

The ^{29}Si NMR spectrum of a sample of polymer with average silicone block length $\bar{n}_{PDMS} = 10$ is shown in Figure 2. Peaks A and A′ correspond to silicon atoms adjacent to polycarbonate blocks. The peaks labeled B and B′ correspond to the second siloxane units into the silicone block and the rest of the internal units under the bulk resonance line (B′).



The silicone block length is calculated directly from eq 1:

$$\bar{n}_{PDMS} = 2\left[\frac{(B + B')}{(A + A')} + 1\right] \quad (1)$$

where A, A', B and B' correspond to the integrated areas under the respective peaks.

The carbon-13 spectrum is, of course, considerably more complex than the ^{29}Si spectrum. Figure 3 shows the ^{13}C spectrum of a polymer which has an average block length of 5 for each block, $(X_5D_5)_n$, and had been prepared in such a fashion that few, if any, isolated BPA units were present (see Experimental Section for details). Peak assignments are shown in the figure. Assignments were made with the assistance of model compounds **6**–**8** and are considered unequivocal. The numbers given with the structures are the chemical shifts in chloroform. The spectrum of **8**, a polymer composed of all dimer units, is shown in Figure 4. This polymer has no "internal" BPA or silicone block units. Thus lines present only in the spectrum of $(X_5D_5)_n$ (Figure 3; peaks numbered 1, 5, 7, 9, 11, and 14) must arise from the internal units.

The resolution of the BPA quarternary carbons into two resonances (11 and 12, Figure 3), internal block and terminal block BPA units, respectively, suggested that *isolated* BPA units incorporated into a silicone chain should also exhibit a chemical shift slightly different from the other two quarternary carbons. To test this idea, a sample of polymer containing only single BPA units, $(BPA\text{-}D_{10})_n$, was prepared and its ^{13}C spectrum was taken. This polymer was then mixed with the sample of $(X_5D_5)_n$ (with no detectable single BPA units) and again examined by ^{13}C NMR. The results are shown in Figure 5. Three BPA quarternary carbons were resolved and are

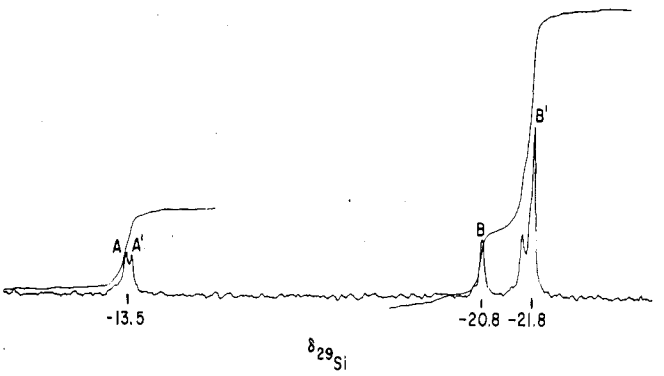


Figure 2. Silicon-29 NMR spectrum of a BPAP–PDMS block copolymer average silicone block length of 10. Chemical shifts are given in ppm relative to internal tetramethylsilane with negative values upfield.

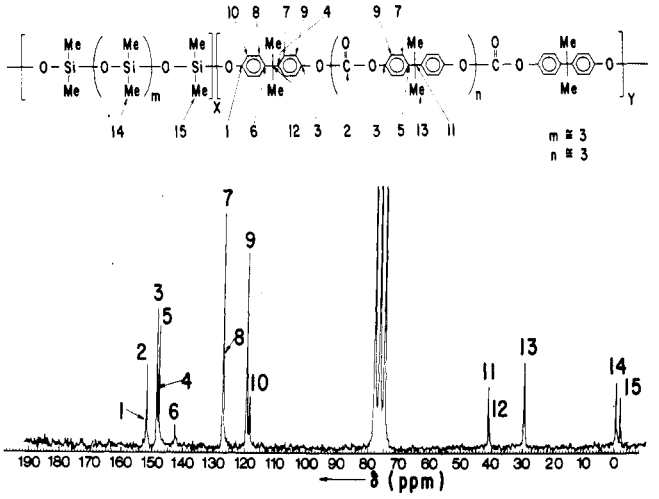
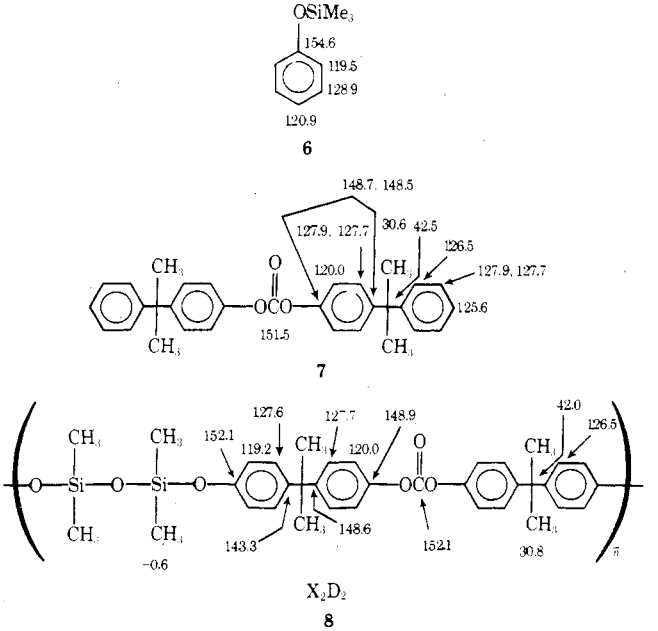


Figure 3. Carbon-13 NMR spectrum of a BPAP–PDMS block copolymer with average block length of five for each block, $(X_5D_5)_n$, in which both internal and terminal block units may be seen. Chemical shifts are given in ppm relative to TMS as calculated from the chloroform-d_1 (δ 76.91) as an internal reference.



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circled in the spectrum. The arrow points to the carbon resonance arising from isolated BPA units. An expansion of the same region for a single polymer with $\bar{n}_{BPAP} \simeq 6$ is shown in Figure 6 with the three types of BPA resonances labeled. In

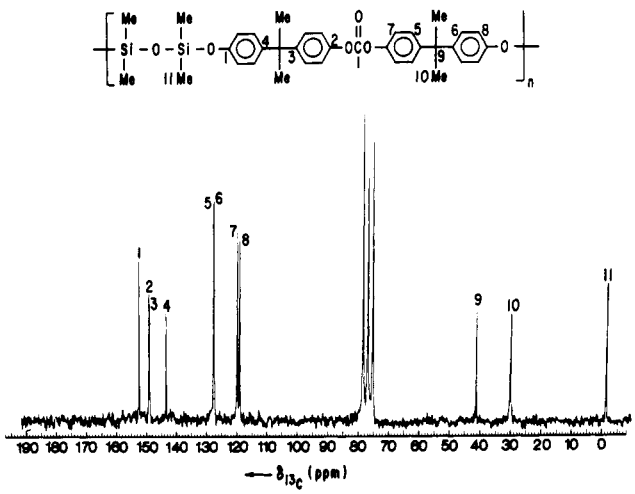
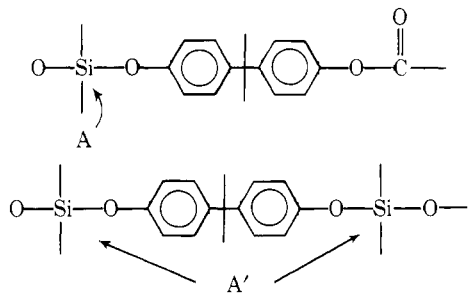


Figure 4. Carbon-13 spectrum of the all dimer copolymers, $(X_2D_2)_n$, in which all resonances correspond to block "terminal" units in the higher polymers.

addition to the quarternary carbons, the presence of isolated BPA units may be detected in the aromatic region (Figure 7). Peaks 2′, 7, and 13 are characteristic only of aromatic carbons in isolated BPA units and are easily distinguishable from the other aromatic resonances.

Perhaps the most surprising result of this study is that the isolated BPA units can also be detected in the ^{29}Si spectrum. Closer examination of Figure 2 reveals that the silicon atoms at the end of the silicon block separate into two closely spaced resonances A and A′. Although the resonances were not fully resolved, it seemed reasonable that the ^{29}Si chemical shift of a silicone moiety adjacent to a polycarbonate block might differ slightly from that adjacent to an isolated BPA unit. This suspicion was confirmed by the observation that the relative intensity of peak A′ increased on the addition of $(BPA\text{-}D_{10})_n$.



Quantitative determinations by ^{29}Si and ^{13}C NMR require extreme caution since both nuclei can have fairly long (>10 s) spin–lattice relaxation times, particularly when nonprotonated. In addition, care must be taken to eliminate differential nuclear Overhauser effects which may occur under proton decoupling conditions and would also give erroneous results. Fortunately, the addition of $Cr(acac)_3$, a paramagnetic relaxation reagent,[6] combined with the use of a gated decoupling sequence to eliminate any residual NOE, as well as a pulse delay, permits accurate integrations for quantitative determinations.

As explained previously, the silicone block length determination from the ^{29}Si peak integrals is reasonably straightforward. An internal check is available from the ^{13}C spectrum (Table I) since the silicon methyl carbons also resolve into two resonances (see Figure 3), one for the dimethylsilicon units at the end of the block (line 15) and one for the internal dimethylsilicon units (line 14). The block length may be calculated by measuring the integrals of each resonance and using

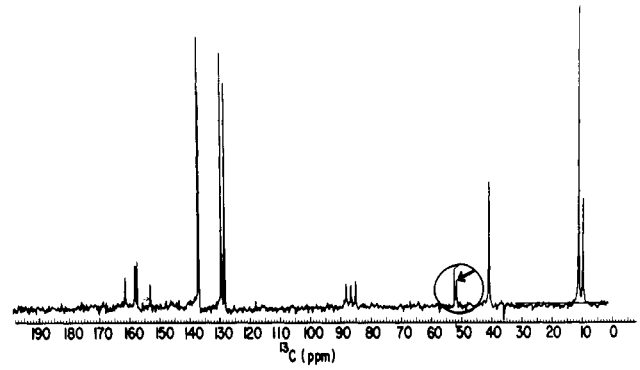


Figure 5. Carbon-13 spectrum of a mixture of $(X_5D_5)_n$ with no isolated BPA units and a polymer containing *only* single BPA units $(BPA\text{-}D_{10})_n$ showing the three different quarternary carbons at ~42 ppm.

eq 1 again, where peak 15 = A + A′ and peak 14 = B + B′. Comparison of the areas under the BPA methyl carbons (line 13, Figure 3) and the silicon methyl carbons (14 + 15) gives the mole ratio of BPA polycarbonate to polysiloxane (i.e., overall polymer composition) directly.

The polycarbonate block length calculation is more indirect since the presence of isolated BPA units must be taken into account. The region of the spectrum corresponding to the BPA quarternary carbons (Figure 6) provides the clearest determination of these units, since all three types of quarternary carbons are baseline resolved and thus reasonably accurate integrals may be obtained. Assuming the area under each peak has been measured and is given by *C*, *D*, and *E* (Figure 6), the average block length of the polycarbonate portion of the polymer may be calculated by taking a weighted average of the block and isolated units as shown by eq 2.

$$\bar{n}_{BPAP} = X_{block}\bar{n}_{block} + X_{isolated}\bar{n}_{isolated} \qquad (2)$$

The formulas for calculating X_{block}, $\bar{n}_{block}$, and $X_{isolated}$ from *C*, *D*, and *E* are shown below:

$$\frac{C+D}{C+D+E} = X_{block} = \text{fraction of total BPA units incorporated into a block >1 unit}$$

$$\frac{E}{C+D+E} = X_{isolated} = \text{fraction of total BPA units which are isolated BPA units}$$

$$2\left(\frac{C}{D}+1\right) = \bar{n}_{block} = \text{av block length for BPA units represented by } C+D \text{ (the rel area of } D \text{ must = 2 since } D \text{ corresponds to one BPA unit at each end of the block)}$$

$$\bar{n}_{isolated} = 1$$

A check on the validity of the NMR integrations was provided by comparison of the analysis of silicone content of the $(X_5D_5)_n$ copolymer by NMR and elemental analysis. Both techniques gave identical results for weight percent silicon in the sample.

The NMR analysis outlined in this paper affords the only direct analysis of these polymer systems and the first means of measuring the concentration of isolated BPA units in the polymer.[8] Efforts are currently underway to apply this technique to a study of the oligomerization reaction as a function of end-capping ratio.

Experimental Section

Sample Preparation. Oligomeric Polydimethylsiloxane Fluids Containing Isolated BPA Comonomer Units. Block copolymers

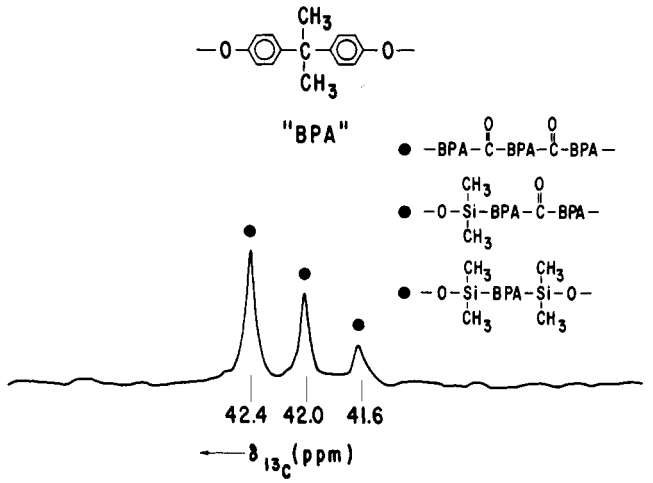


Figure 6. An expansion of the quarternary aliphatic carbon region of the ^{13}C spectrum for a BPAP–PDMS copolymer with average polycarbonate block length, $\bar{n}_{BPAP} = 6$.

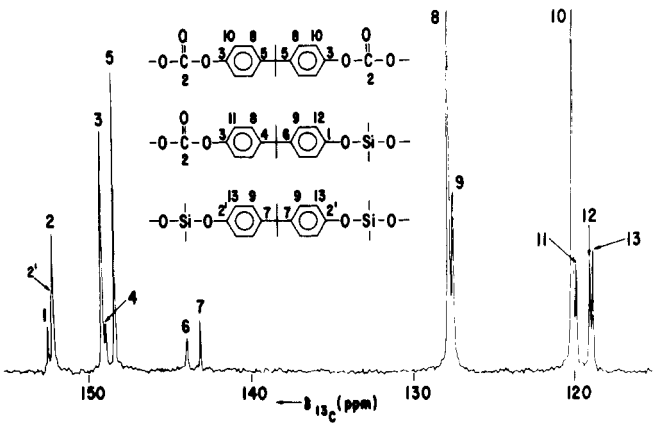


Figure 7. The expanded aromatic region of the ^{13}C spectrum of the same polymer as in Figure 6 showing the fine structure corresponding to internal block, terminal block, and isolated BPA units.

with the structure (BPA-D_{10})$_n$ were prepared directly from BPA and a nominal $ClD_{10}Cl$ fluid as follows: Me_2Cl_2 (200 mL) and 10 mL of distilled pyridine were placed in a reaction flask charged with 12 g of BPA. The solution was rapidly stirred while 40 g of $ClD_{10}Cl$ in 100 mL of Me_2Cl_2 was added (80% rapidly; 20% over a period of 2 h). After stirring for an additional 20 min, 10 g of $ClD_{10}Cl$ in 20 mL of Me_2Cl_2 was added to ensure that no unreacted BPA remained. Precipitation of pyridine hydrochloride was noted. MeOH (2 mL) was added to cap the remaining chlorosiloxane end groups and the Me_2Cl_2 solution was washed five times with a 2% HCl solution and precipitated in H_2O. The material was washed twice more with MeOH and dried under vacuum.

Polymers of the form $(X_2D_2)_n$. $(X_2D_2)_n$ block copolymers were prepared as follows: BPA (50 g, 0.22 mol) was dissolved in 1000 mL of Me_2Cl_2 containing 10 mL of distilled pyridine. Tetramethyldichlorodisiloxane fluid (3.4 g, 0.017 mol) was added with vigorous stirring over a period of 2 h at room temperature. The resulting solution was partially evaporated and then refrigerated for 2 days to crystallize out excess BPA. The concentration and crystallization steps were repeated several times and the reaction mixture was washed with dilute HCl and precipitated. The polymer was taken up in cyclohexane to remove the last traces of BPA, filtered, and reprecipitated. The end-capped fluid was then redissolved in Me_2Cl_2, phosgenated with vigorous stirring, washed with dilute HCl, precipitated in methanol, and dried under vacuum.

Table I
Comparison of ^{13}C and ^{29}Si NMR Determinations of Silicone Block Length[a]

Sample No.	$\bar{n}_{PDMS}(^{13}C)$	$\bar{n}_{PDMS}(^{29}Si)$
1	9.4	9.5
	9.6	
2	9.9	10.2
	10.0	
3	9.5	9.5

[a] Estimated accuracy ±0.2.

Polymers of the form $(X_5D_5)_n$. The $(X_5D_5)_n$ block polymers were prepared directly from a nominal ClD_5Cl fluid using a large excess of BPA in the first reaction step to ensure end-capping was complete and no isolated BPA units were introduced into the polymer chains (see Figure 1). BPA (25 g, 0.11 mol) was dissolved with vigorous stirring in 1000 mL of methylene chloride containing 10 mL of distilled pyridine and 10 g (0.02 mol) of ClD_5Cl. The end-capped fluid and unreacted BPA were subsequently phosgenated with vigorous stirring and the Me_2Cl_2 solution was washed several times with dilute HCl to remove the last traces of pyridine. The polymer was precipitated into methanol and dried under vacuum.

NMR Measurements. The ^{13}C and ^{29}Si Fourier transform NMR spectra were obtained on either a Varian CFT-20 (^{13}C at 20 MHz) or Varian XL-100-15 (^{13}C at 25.2 MHz; ^{29}Si at 19.9 MHz) NMR spectrometer with complete proton decoupling. Deuterated solvents were used for internal field/frequency control (lock). Samples were doped with about 0.1 M tris(acetylacetonato)chromium to shorten the T_1's and suppress the NOE.[7] This was found to be sufficient for the ^{29}Si spectra; spectra obtained with gated decoupling and 10 s pulse delays resulted in identical intregrals. The ^{13}C spectra required the use of a gated decoupling sequence and 2 s pulse delays in addition to the $Cr(acac)_3$ to eliminate any NOE and ensure short relaxation times of all carbon nuclei.

The ^{29}Si spectra were obtained using ~30° flip angles to look at spectral windows of 2000 Hz with 2 s acquisition times. The ^{13}C spectra were obtained with the following parameters: 2 s pulse delay, 5000 Hz (XL-100) or 4000 Hz (CFT-20) spectral width, 30° (XL-100) or 45° (CFT-20) flip angles, and 0.8 s (XL-100) or 1 s (CFT-20) acquisition times. Spectrometer control was achieved with a Varian 620 series computer in all cases (16K core) allowing for 8192 data points and 4096 output data points. Quantitative determinations were made by measuring peak areas with a planimeter and also using the spectrometer integrated intensities for comparison.

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