

Articles

Olefin Polymerization Activity and Crystal Structure of Alkyliron(III) Porphyrin Complexes

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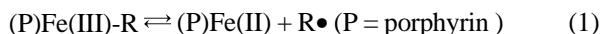
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Alkyliron(III) porphyrins, *n*-butyliron(III) tetraphenylporphyrin, (TPP)Fe-Bu and *n*-butyliron(III) tetrakis(pentafluorophenyl)porphyrin, (F₂₀TPP)Fe-Bu have been evaluated as suitable for olefin free-radical polymerization. Butyl radicals dissociated from *n*-butyliron(III) porphyrin initiated the polymerization reaction, but the ratio of the propagation was low. The GCMS analysis of the reaction mixture of *n*-butyliron(III) porphyrin and styrene has revealed several products containing two butyl groups, while traces of β -hydrogen-abstracted products were observed. The crystal structure of (TPP)Fe-Bu has been determined. The structure of the *n*-butyliron(III) porphyrin reveals the compound containing five-coordinated iron with the average Fe-N distance of 1.973(1) Å and Fe-C of 2.030(2) Å. The iron atom is displaced by 0.137 Å from a four nitrogen mean plane. Crystal system is triclinic, and space group is P-1.

Key Words : Alkyliron porphyrin, Iron(III) porphyrin, Tetrakis(pentafluorophenyl)porphyrin, Radical polymerization, Crystal structure

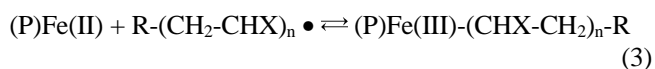
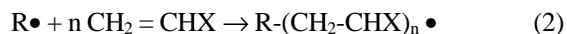
Introduction

Five-coordinate alkyliron(III) porphyrin complexes are relatively unstable, as the iron-carbon bond energy is on the order of 18 kcal/mole.¹ Hence, the complexes undergoing iron-carbon bond homolysis at ambient temperature generate an alkyl radical and an iron(II) porphyrin.²⁻⁶ In the absence of a reactive solvent or other substrates the recombination reaction is favorable, and this process is reversible:



Hence, solutions of alkyliron(III) porphyrins contain small, steady-state free radical concentrations, and this has been termed the "persistent radical effect".⁷⁻⁹

This report describes an initial evaluation of alkyliron(III) porphyrin complexes as possible olefin free-radical polymerization agents. The reversibility observed in equation (1) suggests that a "controlled/living" polymerization system¹⁰ might be devised, in which chain growth is controlled by a recombination of the polymer radical with the iron(II) porphyrin:



Olefin polymerization has been demonstrated in analogous alkylcobalt(III) porphyrin complexes, and controlled/

living polymerization is evident in appropriate combinations of sterically-controlled porphyrins and acrylic ester substrates.¹¹⁻¹⁵ However, substantial differences might exist for the two metals, as the cobalt-carbon bond energy is typically 10 kcal/mole greater than that for the iron-carbon bond in any given porphyrin and alkyl group. Also, as demonstrated in this report, iron(II) porphyrin is less prone to effect β -hydrogen abstraction in the growing polymer radical.

In order to have a thorough understanding of structural factors that may affect reactivity, the (TPP)Fe-Bu was subjected to X-ray crystallographic analysis. Comparisons are made with the previously structured phenyl and methyl complexes.

Experimental Section

General. All manipulations were carried out under vacuum or in a nitrogen-filled inert atmosphere box. Butyl complexes of iron(III), (TPP)Fe-Bu, or iron(III) tetrakis(pentafluorophenyl)porphyrin, (F₂₀TPP)Fe-Bu were generated *in situ* by the addition of a stoichiometric quantity of 1.6 M *n*-butyllithium in hexanes (Aldrich) to the chloroiron(III) porphyrin contained in d₆-benzene.¹⁻⁴ Proton NMR spectroscopy confirmed formation of the butyliron(III) porphyrin. Solid (TPP)Fe-Bu was also prepared by filtration of the reaction mixture to remove LiCl, vacuum concentration to one-fourth volume, and precipitation of the product complex with heptane.

Crystals of (TPP)Fe-Bu suitable for X-ray structure determination were obtained by dissolution of 30 mg of the solid

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complex in 5 mL of benzene with subsequent addition of 5 mL of heptane. This solution in an open beaker in an inert atmosphere box was allowed to evaporate over a period on one day at room temperature. Fine crystals of the presumed iron(II) tetraphenylporphyrin decomposition complex formed on the walls of the beaker, and crystals of the desired butyliron(III) product were taken from the bottom of the beaker after complete evaporation of solvent.

Styrene, methyl methacrylate, and 1-pentene were distilled in a vacuum, and/or passed through an inhibitor removal column (Aldrich) prior to polymerization reactions. In a typical polymerization reaction, 0.20 mL of a 1.46×10^{-2} M butyliron(III) porphyrin in C_6D_6 was mixed with 0.20 mL of a 0.738 M styrene in C_6D_6 in an NMR tube and the tube was sealed in a vacuum. A control sample contained only styrene in C_6D_6 . Samples were maintained at room temperature, 40 °C, 55 °C, or 60 °C and periodically monitored by proton or carbon-13 NMR spectroscopy (at room temperature).

Samples were opened after a period of four days and the contents were subjected to HPLC fractionation on a C-18 column with acetonitrile elution. Excess styrene and iron porphyrin were separated from other products, and the major 260 nm absorbing species appeared as two closely spaced bands. Gas chromatographic mass spectral analysis was performed on a Thermo Finnigan Voyager instrument fitted with a Supelco SPB-1 column using electron-impact ionization.

Structure Determination. A dark purple prism ($0.28 \times 0.17 \times 0.09$ mm) was mounted with grease on the tip of a glass capillary attached to a brass pin with epoxy glue. This was placed on the diffractometer with the long crystal dimension (the b unit cell direction) approximately parallel

to the diffractometer phi axis. Data were collected on a Nonius KappaCCD diffractometer (Mo K-alpha radiation, graphite monochromator) at 190(2) K (cold N_2 gas stream) using standard CCD techniques that yielded 16,081 data. Lorentz and polarization corrections were applied. A correction for absorption using the multi-scan technique was applied ($T_{\max} = 0.9606$, $T_{\min} = 0.8844$). Equivalent data were averaged to yield 8,424 unique data ($R_{\text{int}} = 0.019$, $6985 F > 4\sigma(F)$). Based on preliminary examination of the crystal, the space group P-1 was assigned. The computer programs for the HKLint package were used for data reduction.

The preliminary model of the structure was obtained using XS, a direct methods program. Least-squared refinement of the model vs. the data was performed with the XL computer program. Illustrations were made with the XP program and tables were made with the XCIF program. All are in the SHELXTL v5.1 package. Thermal ellipsoids shown in Figure 1 are at the 35% level unless otherwise noted. All the non-hydrogen atoms were refined with the anisotropic thermal parameters. All H atoms were included with the riding model using the XL program default values. No further restraints or constraints were imposed on the refinement model.

Crystallographic data for the structure reported here has been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-182704 for compound (TPP) Fe-Bu).

Final results: $C_{48}H_{37}FeN_4$, mol. wt. 725.67, $a = 10.9858$ (2) Å, $b = 13.1182$ (2) Å, $c = 14.1746$ (2) Å, $\alpha = 103.2740$ (5)°, $\beta = 105.1140$ (5)°, $\gamma = 101.7200$ (5)°, $V = 1042.69$ (5) Å³, $Z = 2$, $\lambda = 0.71073$ Å, $T = 190$ (2) K, $d_{\text{calcd}} = 1.308$ g/cm⁻³, $\mu = 45.0$ cm⁻¹, $F(000) = 758$, no. of reflections 16081, no. of

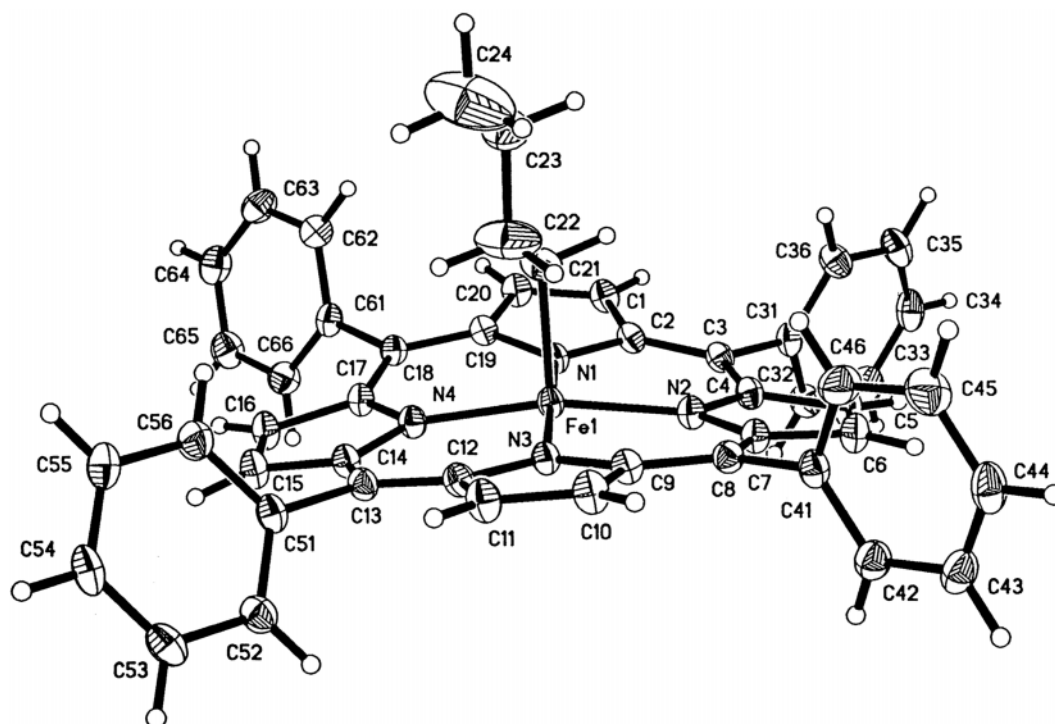


Figure 1. ORTEP drawing of (TPP)Fe-Bu with atomic labeling scheme.

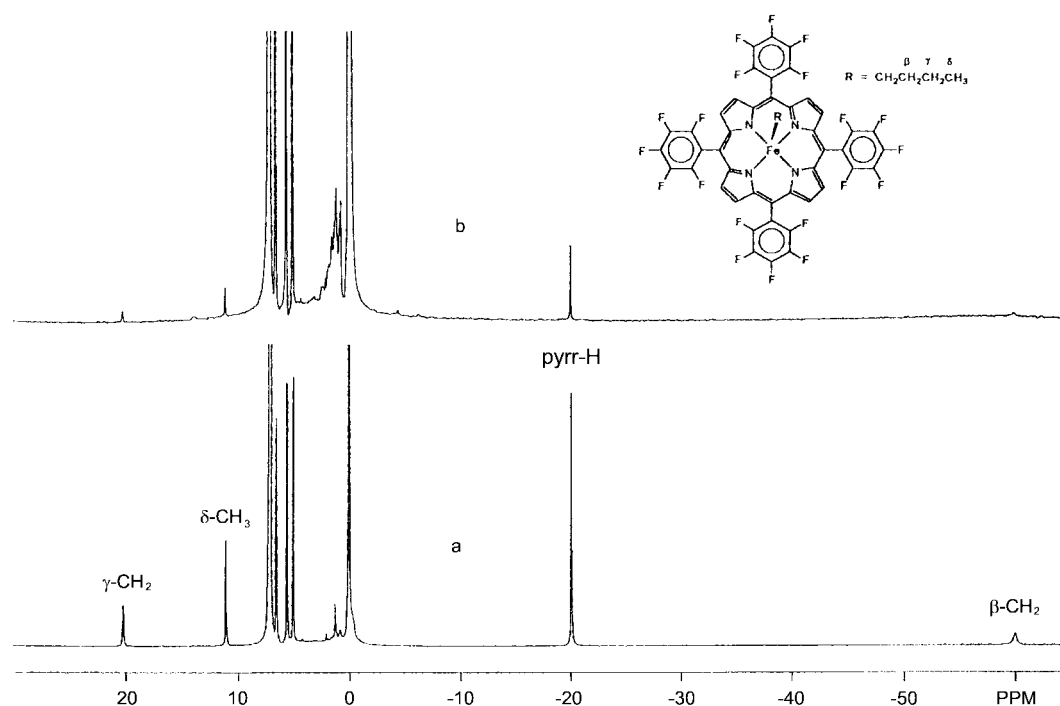


Figure 2. 360 MHz proton NMR spectra of the reaction mixture of $F_{20}TPPFe-Bu$ (0.0730 M) and styrene (0.365 M) in benzene- d_6 . (a) spectrum recorded 30 minutes after mixing (b) spectrum of the solution (a) after 4 days at room temperature.

parameters 480, $R = 0.0386$, $R_w = 0.0993$, crystal system triclinic, space group P-1.

Results and Discussion

Attempted Detection of Polymer-Coordinated NMR Signals. Experiments were designed to evaluate a possible “controlled/living” polymerization chain growth mechanism as described in equation (3). The expectation was that an iron(III)-polymer (oligomer) complex would have a considerably perturbed paramagnetic NMR chemical shift pattern. In particular, the upfield pyrrole proton signal for (TPP)Fe-Bu at -18.0 ppm shows detectable differences among even the methyl, ethyl, butyl ligand series.^{2,4,16-20} The coordinated $\beta-CH_2$ butyl group signal at -64.9 ppm should likewise be significantly different than that for coordinated polymer $\beta-CH$ signals.

Figure 2 shows the proton NMR spectra for a representative reaction mixture of $(F_{20}TPP)Fe-Bu$ and styrene in d_6 -benzene. Spectrum “a” was recorded shortly after mixing the alkene with the alkyliron porphyrin complex. After four days at room temperature spectrum “b” reveals overlapping signals in the aliphatic region due to the formation of oligomer products. This spectrum also shows significant loss in intensity of the -20.1 ppm pyrrole proton signal and has a parallel loss in intensity of the coordinated butyl proton signals at 20.2, 11.1, and -59.9 ppm. The loss of signal intensity reflects conversion of the alkyliron(III) porphyrin to the square-planar iron(II) porphyrin (pyrrole signal at 5.1 ppm). Spectrum “b” is recorded for a reaction mixture, that presumably is undergoing polymerization. However, this

spectrum does not show any significant new paramagnetically-shifted signals that can be attributed to an alkyliron-coordinated growing polymer as described by equation (3). Similar results were obtained, if (TPP)Fe-Bu complex was used and, if methyl methacrylate or 1-pentene was used as substrates. Also, experiments at -53 °C (d_8 -toluene solvent) and 57 °C (d_6 -benzene solvent) with methyl methacrylate substrate revealed no new signals for coordinated alkyl groups. These experiments do not rule out a controlled chain growth mechanism described by equation (3), but if such a process occurs, the iron-coordinated polymer complexes must be a minor species.

An attempt was also made to generate alkyliron(III) porphyrin derivatives from a polymerization reaction initiated by AIBN. Solutions of the iron(II) porphyrin, (TPP)Fe, and 50-fold excess styrene in d_6 -benzene were prepared and excess AIBN was added. Reactions were carried out at room temperature and at 60 °C, and were monitored by proton NMR spectroscopy. However, no -18.0 ppm pyrrole signal was detected for an alkyliron(III) species. Hence, the reaction between the iron(II) porphyrin and a growing polymer radical is either unfavorable, or such adducts represent a very minor equilibrium species. Experiments with the iron(II) porphyrins and alkenes did reveal a potentially complicating aspect for methyl methacrylate as a substrate in any controlled chain growth mechanism. The square-planar (TPP)Fe(II) derivative has a pyrrole proton signal in the 4-5 ppm region for non-coordinating solvents. In d_6 -benzene with 50-fold excess styrene, 1-pentene, or methyl methacrylate the (TPP)-Fe pyrrole proton signal was at 5.1, 4.9, and 8.0 ppm, respectively. The significant downfield shift for the methyl

methacrylate mixture suggests a weak ester group coordination, given an equilibrium mixture of square-planar and five- or six-coordinate iron(II) porphyrin complexes. Hence, substrate coordination potentially competes with iron(II) uptake of the growing polymer radical as described in equation (3).

The absence of detectable signals in NMR for a polymer-bound iron(III) porphyrin species may be rationalized by the expected lability of a sterically-demanding secondary carbon alkyl complex. Bond dissociation energies for alkylcobalt(III) porphyrin show differences of 8 kcal/mole for the primary vs. secondary carbon complexes. Hence, if the iron-carbon bond energy for (TPP)Fe-Bu is 18 kcal/mole, a complex made from a poly-olefin growing chain could have a bond energy as low as 10 kcal/mole.¹

In comparison, Wayland *et al.* reported alkylcobalt(III) porphyrin polymerization study, in which acrylic ester polymer bound cobalt porphyrin species were observed in ¹H nmr and those showed the controlled/living polymerization.^{12,14} The difference between two metal porphyrins might come from the metal-carbon bond energies. The bond energy of the cobalt-carbon is typically 10 kcal/mole greater than that for the iron-carbon.¹

Analysis of Reaction Mixtures. Styrene, methyl methacrylate, and 1-pentene polymerization reactions were attempted as described in the previous section with (F₂₀TPP)Fe-Bu concentrations approximately 1 mM and the alkene concentrations from 5 to 100 times in molar excess. Proton NMR spectral monitoring of alkene signals for the reaction mixture of (F₂₀TPP)Fe-Bu and styrene revealed only a few percent consumption of the parent alkene, with the appearance of additional overlapping NMR signals in the aliphatic region, as seen in Figure 2b. Following HPLC fractionation of the reaction mixtures, to remove excess styrene and iron porphyrin, the volatile components were analyzed by GCMS. Polymerization reaction temperatures of 25 °C, 40 °C, and 55 °C were used. Table 1 summarizes the volatile products identified in significant quantities. Even at room temperature, some oligomeric products were produced, since radical from *n*-butyliron(III) porphyrin was produced and initiated at the room temperature. Yields were, however, not much improved at higher temperature. None of these products were found in blank reaction mixtures, in which (F₂₀TPP)Fe-Bu was omitted.

All the identified products result from butyl radical

Table 1. Products from (F₂₀TPP)Fe-Bu Polymerization of Styrene

Product	mass	25 °C	40 °C	55 °C
Bu-CH=CHf	160	tr	tr	tr
Bu-CH ₂ -CHφ-Bu	218	sig	sig	sig
Bu-CH ₂ -CHφ-CH ₂ -CH ₂ φ	266	tr	sig	sig
Bu-CH ₂ -CHφ-CH=CHφ	264	not det	not det	tr
Bu-CH ₂ -CHφ-CH ₂ -CHφ-Bu	322	sig	sig	sig
Bu-CH ₂ -CHφ-CH ₂ -CHφ-CH ₂ -CHφ-Bu	426	sig	sig	sig

Reaction times, 4 days. Initial concentrations, (F₂₀TPP)Fe-Bu, 0.0074 M; styrene 0.37 M. tr = trace product, sig = significant product; not det = not detected.

Table 2. Atomic coordinates (×10⁴) and Equivalent isotropic displacement parameters (Å² × 10³) for (TPP)Fe-Bu

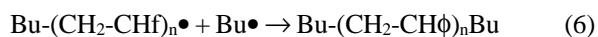
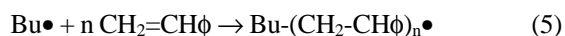
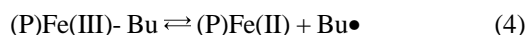
	x	y	z	U(eq) ^a
Fe1	3269(1)	3718(1)	7879(1)	24(1)
N1	2831(1)	5065(1)	7702(1)	25(1)
N2	1377(1)	2934(1)	7378(1)	27(1)
N3	3688(1)	2388(1)	8124(1)	25(1)
N4	5085(1)	4580(1)	8679(1)	27(1)
C1	1727(2)	6235(1)	7102(1)	31(1)
C2	1604(2)	5179(1)	7259(1)	27(1)
C3	420(2)	4403(1)	7016(1)	27(1)
C4	325(2)	3350(1)	7086(1)	28(1)
C5	-892(2)	2514(2)	6756(2)	34(1)
C6	-590(2)	1573(2)	6801(2)	35(1)
C7	816(2)	1829(1)	7184(1)	29(1)
C8	1504(2)	1063(1)	7294(1)	27(1)
C9	2856(2)	1338(1)	7730(1)	28(1)
C10	3589(2)	558(1)	7868(2)	34(1)
C11	4856(2)	1130(1)	8362(2)	34(1)
C12	4920(2)	2268(1)	8532(1)	27(1)
C13	6056(2)	3120(1)	9049(1)	27(1)
C14	6100(2)	4212(1)	9161(1)	28(1)
C15	7246(2)	5104(2)	9727(2)	35(1)
C16	6970(2)	6012(2)	9549(2)	34(1)
C17	5635(2)	5689(1)	8876(1)	28(1)
C18	5029(2)	6368(1)	8418(1)	27(1)
C19	3705(2)	6053(1)	7847(1)	26(1)
C20	3016(2)	6765(1)	7445(1)	31(1)
C21	3562(2)	3411(2)	6497(2)	42(1)
C22	4269(3)	2604(3)	6226(2)	73(1)
C23	4410(2)	2409(2)	5183(2)	52(1)
C24	5117(5)	1563(4)	4938(3)	126(2)
C31	-834(2)	4698(1)	6641(1)	29(1)
C32	-1370(2)	5201(2)	7337(2)	37(1)
C33	-2537(2)	5462(2)	6994(2)	44(1)
C34	-3164(2)	5231(2)	5960(2)	43(1)
C35	-2637(2)	4734(2)	5262(2)	42(1)
C36	-1472(2)	4467(2)	5602(2)	37(1)
C41	747(2)	-121(1)	6904(1)	29(1)
C42	65(2)	-604(2)	7457(2)	36(1)
C43	-641(2)	-1697(2)	7071(2)	40(1)
C44	-679(2)	-2314(2)	6137(2)	42(1)
C45	-8(2)	-1846(2)	5579(2)	50(1)
C46	710(2)	-750(2)	5965(2)	43(1)
C51	7312(2)	2857(1)	9477(1)	30(1)
C52	7501(2)	2442(2)	10302(1)	34(1)
C53	8673(2)	2209(2)	10698(2)	40(1)
C54	9653(2)	2370(2)	10263(2)	41(1)
C55	9470(2)	2770(2)	9433(2)	44(1)
C56	8304(2)	3022(2)	9047(2)	40(1)
C61	5834(2)	7492(1)	8549(1)	29(1)
C62	6030(2)	7785(2)	7705(2)	36(1)
C63	6778(2)	8823(2)	7821(2)	41(1)
C64	7341(2)	9578(2)	8778(2)	43(1)
C65	7147(2)	9301(2)	9619(2)	44(1)
C66	6391(2)	8267(2)	9506(2)	37(1)

^aU(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for (TPP)Fe-Bu

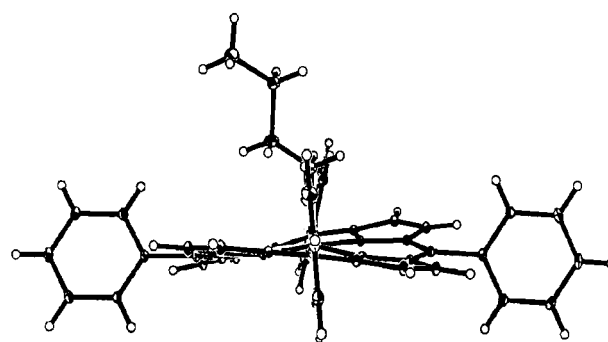
Bond lengths (Å)			
Fe1-N4	1.964(1)	Fe1-C21	2.030(2)
Fe1-N1	1.975(1)	C21-C22	1.475(3)
Fe1-N3	1.975(1)	C22-C23	1.497(3)
Fe1-N2	1.977(1)	C23-C24	1.506(4)
Bond Angles (deg)			
N4-Fe1-N1	89.66(6)	N4-Fe1-C21	95.90(8)
N4-Fe1-N3	90.16(6)	N1-Fe1-C21	89.77(7)
N1-Fe1-N3	177.01(6)	N3-Fe1-C21	93.22(7)
N4-Fe1-N2	166.99(6)	N2-Fe1-C21	97.11(8)
N1-Fe1-N2	89.86(6)	C22-C21-Fe1	119.60(2)
N3-Fe1-N2	89.65(6)	C21-C22-C23	116.0(2)
		C22-C23-C24	113.8(2)

addition to styrene, and the surprising result is that several products contain two butyl groups. Hence, it appears that after the initiation reaction, the free radical polymerization is frequently terminated by reaction with a second butyl radical:



The $Bu-CH_2-CH\phi-CH_2-CH_2\phi$ product results from the combination of one butyl radical and two styrene monomers, with quenching, by either hydrogen atom abstraction or disproportionation of two radicals. Likewise, the trace alkene products, $Bu-CH=CH\phi$ and $Bu-CH_2-CH\phi-CH=CH\phi$, likely result from radical disproportionation reactions. It should be noted that larger, non-volatile oligomers would not have been detected in the GCMS analysis. And, in experiments where the HPLC fractions were placed under a high vacuum, no significant residue was present, which would allow for the proton NMR detection of polymer signals. According to the mass results of the reaction mixture, β -hydrogen abstraction unfavorably occurred from growing polymer radicals in the presence of the iron porphyrin because of ligand steric hindrance. That is the promising advantage for the process of "controlled/living" radical polymerization. It had been also observed in analogous alkylcobalt poporphyrin work.^{12,14}

Synthesis and Crystal Structure of (TPP)Fe-Bu. Alkyl- and aryliron(III) porphyrin complexes are readily prepared under anaerobic conditions through addition of Grignard or lithium alkyl/aryl agents to the chloroiron(III) porphyrin contained in an inert solvent.²⁻⁴ However, five-coordinate alkyliron(III) complexes are extremely unstable in air, turning into oxo-bridged dimeric complex. Even in an inert atmosphere, those unstable complexes undergoing iron-carbon bond homolysis at ambient temperatures generate an alkyl radical and the iron(II) porphyrin.^{5,6} Due to this instability there are insufficient reports for the crystal structure of the alkyliron(III) porphyrins complexes. Phenyliron(III)

**Figure 3.** Side view of the (TPP)Fe-Bu showing the ruffling of the porphyrin ring and the *n*-butyl chain.

tetraphenylporphyrin, (TPP)Fe-Ph,²¹ methyl and acyl compound of iron(III) tetra-*p*-anysylporphyrin, (TAP)Fe-Me and (TAP)Fe-C(O)(*n*-butyl)²² have been previously structured.

The crystal structure of (TPP)Fe-Bu is shown in Figure 1. Atomic positional parameters are listed in Table 2, while selected bond distances and bond angles are listed in Table 3.

The iron is five-coordinate in the complex and the structural parameters are consistent for low-spin iron(III) as well as the NMR spectroscopic results. The average distance of the iron-nitrogen bond is 1.973(1) Å, which is similar to those in (TAP)Fe-Me (TAP, the anion of tetra-*p*-anisylporphyrin)²² and (TPP)Fe-Ph²¹ with the values of 1.967 and 1.962 Å. The iron-nitrogen distance is shorter for the low-spin iron(III) complex than 2.069(8) Å averaged value of the high-spin iron(III) porphyrin complex.²³⁻²⁴ The difference is caused from non-populating dx^2-y^2 orbital in low-spin iron complex. The iron atom is raised 0.137(0.001) Å from a four-nitrogen plane. This distance is slightly shorter than methyl analogue with a value of 0.17 Å and 0.146 Å of phenyl complex. The structural parameters are consistent for five-coordinate low-spin iron(III) as well as the NMR spectroscopic results.

The axial *n*-butyl group bound to the iron shows a zigzag conformation as shown in Figure 3. The bond distance of Fe and α -carbon in the butyl chain is 2.030(2) Å, which is longer than the 1.979(9) Å of TAP methyl compound, (TAP)Fe-Me.²² These distances are expected to be longer than the iron- sp^2 carbon in corresponding phenyl or acyl complexes, (TPP)Fe-Ph,²¹ and (TAP)Fe-C(O)(*n*-Bu),²² 1.955(3), and 1.965(1) Å, respectively. The C-C distances in the butyl group are shown in Table 3, which are normal for the organometallic alkyl group.²²

The porphyrin ring is ruffled as shown in Figure 3, which might be due to the contraction of the core and the shortness of Fe-N bonds. Rufflings were also found in previous methyl and phenyl analogues.^{21,22} The porphyrinato phenyl rings show normal geometry and are nearly perpendicular to the porphyrin ring with dihedral angles of 78.83, 85.46, 89.77 and 80.06°. Unusual intermolecular contacts are not observed.

Conclusion

Butyl radical from the alkyl-iron(III) porphyrins, (TPP)Fe-

Bu and (F₂₀TPP)Fe-Bu, initiated polymerization and some propagated oligomers were produced. Several identified products contained two butyl groups, while trace of β -hydrogen abstracted products were observed. Very weak iron-carbon in the alkyl-iron(III) porphyrins system resulted in fast termination in polymerization reactions with butyl radical. No signal observation in NMR for the iron-polymer growing radical may come from the weak bond property.

Crystal structure of (TPP)Fe-Bu contained five-coordinated iron(III) with the average Fe-N distance of 1.973(1) Å and Fe-C of 2.030(2) Å. The porphyrin plane was ruffled and the iron atom was displaced by 0.137 Å from a four nitrogen mean plane. The axial butyl group was coordinated to iron resulting in low spin state.

Although, up to now it is hard to define that alkyliron(III) porphyrin is a good "controlled/living" radical polymerization catalyst, this initial work for understanding the alkyl-iron porphyrin-catalyzed polymerization should guide further research to design a "controlled/living" radical polymerization catalyst with new alkyliron(III) porphyrins containing a moderately weak iron-carbon bond, and to choose a suitable monomer.

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