Radical Copolymerization of Styrene with Ferrous and Ferric Protoporphyrin IX Derivatives and the Effect of Ligand Complexation

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Received August 30, 1982

ABSTRACT: The copolymerization of styrene with various iron porphyrin derivatives has been studied as a function of reaction time for yield, iron porphyrin content in the copolymer, and molecular weight. Both ferrous and ferric protoporphyrin IX dimethyl esters (Fe^{II}HDME and Fe^{III}HDME) strongly retard polymerization as compared to the homopolymerization of styrene in the absence of HDME. In contrast to the current belief that the vinyl groups of iron protoporphyrin cannot be copolymerized with other vinyl monomers, we show that this inhibition can be eliminated by proper ligation of the iron. In the presence of strong axial ligands, i.e., Fe^{III}HDME·$(CN)_2$, Fe^{II}HDME·$(IM)_2$ (IM = 1-methylimidazole), and Fe^{II}HMDE·CO, this retardation effect is eliminated. The molecular weight does not change with increasing Fe^{II}HDME·CO content in the copolymerization feed mixture while the number of iron porphyrins per styrene in the copolymers increases linearly. This is interpreted as evidence that Fe^{II}HDME·CO is incorporated within the polymer chain and does not act as a chain terminator as previously reported. Copolymerization of styrene with ferric protoporphyrin IX bis[3-(1-imidazolyl)propylamide] (HDA) shows, during early stages of the reaction, anomalously large incorporation of HDA into the polymer (10 mol % of HDA in the copolymer for a feed of 0.14 mol % of HDA), lowered yield, and reduced molecular weight. Complexation of Fe^{II}HDA with CO allows polymerization to proceed normally, with yield, iron porphyrin content, and molecular weight analogous to those for the styrene–Fe^{II}HDME·CO copolymerization.

Hemoglobin and myoglobin transport oxygen via an iron(II) porphyrin (heme) group that is axially ligated to the globin through the proximal F8 histidine residue. The globin protects the heme from oxidation by providing a rigid, hydrophobic environment, thus preventing proton-facilitated electron transfer from the iron(II) to the bound oxygen molecule.[1] Also, contact between heme groups and subsequent oxidation to the μ-oxo dimer are eliminated due to the rigid, sterically hindering nature of the globin.[2]

Synthetic polymers containing iron porphyrins may be useful models of oxygen transport in hemoglobin. The first successful experiment to bind oxygen reversibly in such a system was reported by Wang.[3] He embedded heme and 1-(phenylethyl)imidazole in a matrix of polystyrene and found this heme to be stable to oxidation for several days. Copolymers of styrene and vinylimidazole allowed reversible oxygenation of metalloporphyrins coordinated to the polymer in the solid state.[4] The rate of oxygenation and ligand-exchange reactions in these models depended on the gas permeability of the polymer matrix, which was significantly slower than in homogeneous solution.[5]

Incorporation of a heme unit into the backbone of the polymer chain enhances polymer–heme interactions, which may provide the hydrophobic, sterically protected environment necessary to prevent oxidation of the ferrous iron. Lautsch et al.[6,7] reported the first radical polymerization of protoporphyrin through the 2,4-vinyl groups. Protoporphyrins have been copolymerized with a variety of monomers with iron insertion subsequent to polymerization.[8] The synthesis of these copolymers is difficult, and strongly acidic conditions are necessary for iron insertion. More recent work by Fuhrhop et al.[9] showed that the terpolymers of styrene, 1-vinylimidazole, and heme dimethyl ester (HDME) undergo reversible oxygenation in the solid state but oxidation of Fe(II) occurs within several seconds in organic solvents at room temperature. Nishide and co-workers[10] attempted to further define the polymerizability of HDME and concluded that HDME acts as a chain terminator in copolymerization with styrene but may be incorporated in the polymer chain when vinylimidazole is a termonomer. They proposed that termination occurs through a radical transfer from the vinyl group to the central iron atom. Castro et al.[11] have shown that free radical polymerization initiators undergo redox reactions with iron octaethylporphyrin in both the Fe(II) and Fe(III) states.

It appears that iron porphyrins can act as inhibitors of free radical polymerization; however, the mechanism of chain termination is unclear. The central objective of this work is to resolve the apparently conflicting observations described above and propose a means to eliminate the termination reaction. The present results show the role of iron protoporphyrin derivatives as comonomers or retarders in free radical polymerization as a function of the number and type of axial ligand on the iron and the oxidation state.

Experimental Section

Materials. Styrene (S) and dimethylformamide (DMF) were distilled under reduced pressure before use. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Hemin (Sigma Chemical Co.) was converted to the dimethyl ester (HDME) with a procedure adapted from Falk.[12] Hemin bis[3-(1-imidazolyl)-propylamide] (HDA) was synthesized by procedures outlined by Traylor and co-workers.[13]

Polymerizations. The same general copolymerization procedure was used throughout this work and is given below in detail for styrene and hemin dimethyl ester. Any variations in this procedure, methods of ligand addition, and oxidation or reduction are given subsequently.

In a polymerization tube with a side arm were placed 9.0 mL of styrene (0.078 mol), 18.0 mL of DMF, 0.045 g of AIBN (7.8×10^{-4} mol), and 0.075 g of HDME (1.1×10^{-4} mol). This tube was sealed with a crown cap and neoprene gasket and degassed by four cycles of freezing and evacuation followed by thawing. The vessel was filled with nitrogen and placed in a bath at 60 °C. An aliquot was removed from the mixture by syringe at 1-h intervals under a steady nitrogen stream. A 2.0-mL volume of this aliquot was eluted through a Biobeads SX2 column (Bio-Rad Corp.) in benzene, which cleanly separated the copolymer from the unreacted monomers. This column purification method yielded ligand-free, oxidized iron porphyrin/styrene copolymers.

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The polymer fraction was freeze dried in a preweighed flask and then further dried at 60 °C in vacuo for 48 h.

Polymer composition was determined by UV/visible spectroscopy using a Cary 14 recording spectrophotometer. Two methods, which gave consistent results, were used. If sufficient polymer was obtained for accurate weighing, hemin content was found by Beer's law. Polymerization of the porphyrin vinyl group causes a shift in the Soret maximum from 388 to 383 nm for HDME. Extinction coefficients, ϵ, were determined by weighing for the monomers and assumed to be equivalent with those in the polymer, with $\epsilon_{388}(Fe^{III}HDME) = 90\,000\ M^{-1}\ cm^{-1}$ and $\epsilon_{409}(Fe^{III}HDA) = 47\,800\ M^{-1}\ cm^{-1}$. Alternatively, the ratio of hemin to styrene in the copolymer was determined from the ratio of absorbances, with ϵ_{269}(polystyrene) = 186 $M^{-1}\ cm^{-1}$.

Molecular weight was determined with a Waters Model 201 gel permeation chromatography calibrated with polystyrene standards, with either tetrahydrofuran or chloroform solvent.

Copolymerizations are coded below in a S/HDME·X*N* format, where S/H designates styrene/hemin copolymer, DME or DA refer to the hemin derivative, X is the ligand, and *N* is the time, in hours, at which an aliquot was taken.

S/Fe^{II}HDME. The S/Fe^{III}HDME reaction mixture was titrated with aqueous dithionite to the reduced species, indicated by a visible shift from 570 to 552 nm.

S/Fe^{III}HDME·(CN)$_2$. The S/Fe^{III}HDME reaction mixture was titrated with either concentrated aqueous KCN (using the λ_{max} = 431 nm absorption band for the dicyanide complex) or a filtered solution of 0.59 g of 18-crown-6 (Aldrich), 0.13 g of KCN, and 10.0 mL of DMF. Additional DMF was added after the end point was reached to give a total volume of 18.0 mL. Both methods gave cyanide derivatives that behaved identically in copolymerization.

S/Fe^{III}HDME·(IM)$_2$. To the S/Fe^{III}HDME reaction mixture was added a 230-fold excess of 1-methylimidazole (IM). Visible spectra of the initial reaction mixture (λ_{max}[HDME·(IM)$_2$] = 407 nm) showed the HDME to be approximately 50% unligated, but with progression of the polymerization all iron porphyrins became six-coordinated, with a color change from brown to red, indicative of the formation of Fe^{II}HDME·(IM)$_2$. The red color was lost upon exposure to air.

S/Fe^{II}HDME·CO. Carbon monoxide was bubbled through the S/Fe^{II}HDME reaction mixture to yield a cherry red solution (λ_{max} = 411 nm).

S/Fe^{III}HDA. Polymerization was identical with that of S/Fe^{III}HDME except that an equimolar quantity of HDA replaced the HDME (λ_{max} = 409 nm).

S/Fe^{II}HDA·CO. To the S/HDA reaction mixture was added 100 μL of acetic acid, aqueous dithionite and then the mixture was saturated with CO (λ_{max} = 419 nm).

S. Styrene was homopolymerized for reference purposes; the procedure for copolymerization was followed except for omission of the iron porphyrin monomer.

A series of S/HDME·CO polymers with varying HDME contents was prepared as follows: 2.76 mL of styrene (0.024 mol), 0.0394 g of AIBN (0.00024 mol), and 0.5 mL of DMF and HDME with a HDME/S × 10^4 molar ratio equal to 0, 2.5, 5, 7.5, and 10. Each sample was degassed and a constant volume of concentrated aqueous sodium dithionite added. After thorough flushing with carbon monoxide, the cherry red reaction mixtures was placed in a 60 °C bath for 6 h. Polymers were precipitated into methanol three times and dried at 60 °C in vacuo for 48 h.

Results and Discussion

Polymerization and Polymer Composition. Polymerization yield as a function of time for formation of polystyrene in the presence and absence of HDME is shown in Figure 1. The presence of iron porphyrin in either the Fe(II) or Fe(III) state retards the polymerization rate significantly, with very little polymer being formed within 4 h. In the absence of iron porphyrins, styrene has a very rapid rate of polymerization. Initially, a Fe^{III}HDME is incorporated almost threefold faster than Fe^{II}HDME and the iron porphyrin is enriched in the polymer about eightfold over the feed composition.

The retardation effect may be explained on the basis of

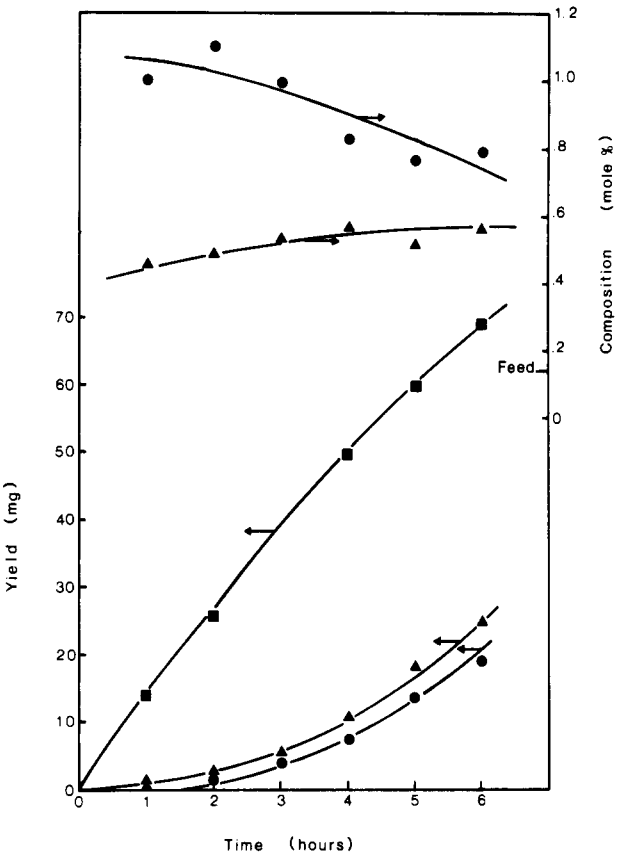


Figure 1. Polymer yield vs. time for (■) polystyrene, (▲) S/Fe^{II}HDME, and (●) S/Fe^{III}HDME. Reaction conditions were identical and are given in the text. No strong ligands are present. Inset is mol % HDME in polymer as a function of time for S/Fe^{II}HDME and S/Fe^{III}HDME.

the mechanism proposed by Castro[11] of the reaction of hemin derivatives with free radicals. For Fe(III) porphyrins, axial inner-sphere reduction to Fe(II) is followed by radical–ligand combination:

$$R\cdot + \overset{|}{Fe}^{3+}Cl \longrightarrow RCl + \overset{|}{Fe}^{2+} \qquad (1)$$

On the other hand, Fe(II) porphyrins were found to be oxidized:

$$R\cdot + \overset{|}{Fe}^{2+} \xrightarrow{H^+} \overset{|}{Fe}^{3+} + RH \qquad (2)$$

Reactions 1 and 2 allow iron to cycle between its two oxidation states until the source of radicals is consumed. The radical concentration and its relation to the retardation of polymerization are discussed below. The high reactivity of the porphyrin vinyl group causes the observed iron porphyrin enrichment in the copolymer. This enhanced reactivity may be attributed to the resonance-stabilized nature of the porphyrin macrocycle in conjugation with the vinyl groups. This is supported by Nishide's observation that porphyrin vinyl groups do not copolymerize with unconjugated monomers.[10]

If reactions 1 and 2 had very high rates, then HDME would completely prevent polymerization. It appears that polymerization is competitive with these modes of chain termination; thus these four-coordinate iron protoporphyrins act as retarders rather than as inhibitors. This picture is consistent with the results of Nishide et al.,[10] who copolymerized styrene with Fe^{III}HDME in varying amounts. They found a decrease in molecular weight with increasing iron protoporphyrin concentration, which would

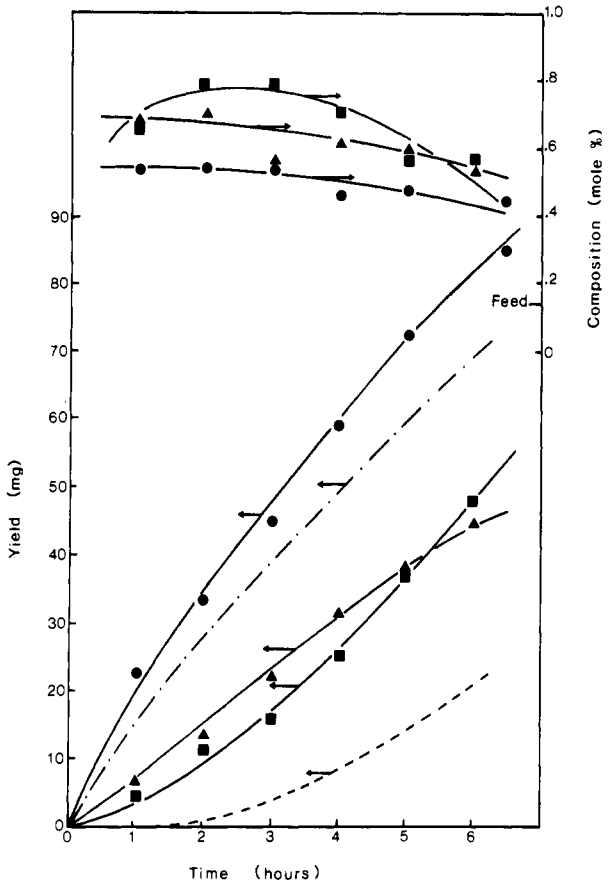


Figure 2. Polymer yield vs. time for various ligated HDME monomers copolymerized with styrene under identical reaction conditions: (-·-) polystyrene; (---) S/Fe^{III}HDME; (●) S/HDME·CO; (▲) S/HDME·CN; (■) S/HDME·IM. Inset is mol % HDME in copolymers as a function of time.

be expected for an iron protoporphyrin behaving as a chain-terminating agent in the polymerization.

If the retardation of free radical polymerization by iron protoporphyrins occurs through the proposed inner-sphere mechanism, strong ligands in the fifth and sixth coordinated positions should eliminate the retardation by blocking direct access to the iron atom. We have chosen to study copolymerization of styrene with Fe^{III}HDME with cyanide and 1-methylimidazole ligands and copolymerization of styrene with Fe^{II}HDME·CO. For these cases polymer yield and hemin content in polymer as a function of time are shown in Figure 2 and compared with the yield of polystyrene in the absence of any iron porphyrin complex. All three cases show a dramatic increase in copolymerization rate compared to the rate for iron protoporphyrins without strong ligands. Cyanide eliminates the retardation and greatly increases the initial polymerization rate to about half of that for styrene homopolymerization. S/Fe^{II}HDME·CO shows no sign of retardation and even has a slightly higher rate of polymerization than styrene alone. Initially, the S/Fe^{III}HDME·(IM)$_2$ case behaves similarly to the S/Fe^{III}HDME·(CN)$_2$ case except the former polymerization rate curve has a concave-upward shape with respect to the x axis, as in the S/Fe^{III}HDME curve, which suggests that there is some four-coordinate hemin present. This is supported by the optical spectra of the initial reaction mixture. As the Fe(III) is converted to Fe(II), the binding of imidazole to the hemin is presumably more complete and the slope of the curve becomes identical with that for S/HDME·CO.

The change in slope of the S/HDME·(IM)$_2$ curve occurs after about 3.5 h. If one assumes each radical is terminated

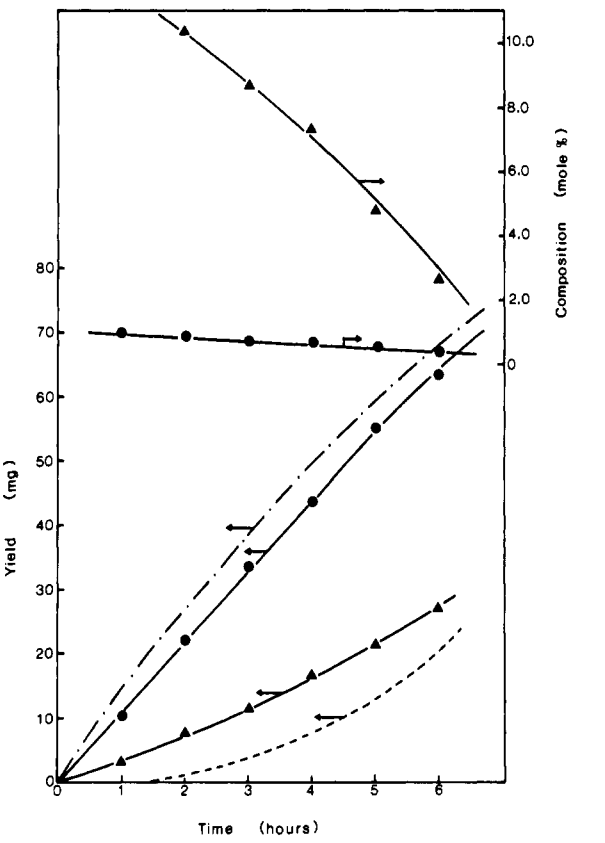


Figure 3. Polymer yield vs. time for derivatives of iron protoporphyrin IX bis[3-(1-imidazolyl)propylamide]: (-·-) polystyrene; (---) S/Fe^{III}HDME; (▲) S/HDA; (●) S/HDA·CO. Inset is mol % HDA in the copolymers as a function of time.

by contact with an iron, then the moles of radicals generated over this time period should equal the moles of Fe^{III}HDME. The expression for the rate of initiation is

$$R_i = 2fk_d[I] \quad (3)$$

where $k_d = 8.5 \times 10^{-6}$ s^{-1},[14] $f = 0.7$,[15] and [I] $= 2.89 \times 10^{-2}$ M. Then $R_i = 3.93 \times 10^{-7}$ M s^{-1} and $R_i t = 4.2 \times 10^{-3}$ M at $t = 3$ h as compared to the total amount of HDME in the reaction mixture of 4.07×10^{-3} M. Therefore the total number of radicals generated is approximately equal to the number of hemins that are reduced by reaction with these radicals after 3 h. The rate of polymerization does not appear to have a dependence on the type of ligand for a given oxidation state. One would expect the polymeric product of the S/HDME·(IM)$_2$ reaction to have a larger range of molecular weights due to the steadily decreasing amount of chain-transfer agent (i.e., unchelated iron) present as will be discussed later.

The composition vs. time data given in Figure 2 show a significant enrichment of iron porphyrin in the copolymer as seen previously, with no apparent effect of ligand on the reactivity of HDME. The percent HDME in the polymer decreases slowly over time due to depletion of the iron protoporphyrin from the reaction mixture. In the CN$^-$ case, 9% of the total hemin has been consumed after 2 h and 27% has been consumed after 6 h.

Fe(II) protoporphyrin IX bis[3-(1-imidazolyl)propylamide] (HDA) is a promising monomer in the synthesis of a polymer that may bind oxygen reversibly and also is interesting in this investigation because two strong ligands are covalently bound to the macrocycle.[16,17] The results for copolymerization of styrene and HDA are shown in Figure 3. The polymerization rate for S/Fe^{III}HDA, though linear and thus not showing typical retardation behavior of the four-coordinate hemins, is markedly depressed

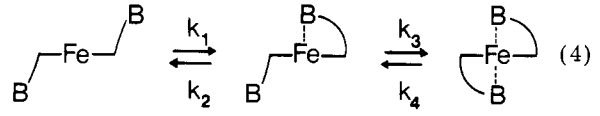
Table I
Molecular Weight Data for Styrene/Iron Porphyrin Copolymers Determined by Gel Permeation Chromatography in THF

sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	hemins/chain	mol % hemin
A. Molecular Weight of Polystyrene vs. Molecular Weights of S/HDME·X Copolymer					
PS·6	16 300	39 500	2.43		
S/HDME·CO6	13 900	30 000	2.12	0.56	0.44
S/HDME·CN6	10 400	25 900	2.49	0.54	0.53
S/HDME·IM6	4 300	19 900	4.62	0.26	0.56
B. Molecular Weights of S/HDME·CO Copolymers					
S/HDME·CO4	13 900	30 000	2.16	0.56	0.45
S/HDME·CO6	14 900	32 000	2.21	0.64	0.44
S/HDME·CO24	15 600	41 800	2.67	0.46	0.31
C. Molecular Weights of S/HDA and S/HDA·CO Copolymers					
S/HDA·6	6 400	18 000	2.81	1.35	2.62
S/HDA·24	12 200	25 900	2.12	0.75	0.67
S/HDA·CO4	10 200	24 800	2.42	0.69	0.61
S/HDA·CO6	9 800	24 000	2.46	0.48	0.44

Table II
Molecular Weight Data for S/HDME·CO Copolymers with Varying Heme Concentrations Determined by Gel Permeation Chromatography in Chloroform

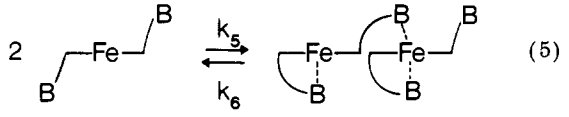
feed HDME/S × 10^4	polymer HDME/S × 10^4	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	hemes/chain
0	0	32 800	65 000	1.98	
2.5	4.6	30 800	66 200	2.15	0.136
5	8.6	28 900	64 600	2.24	0.237
7.5	13.4	30 400	65 400	2.15	0.388
10	17.5	30 800	77 500	2.52	0.507

compared to the rate with cyanide or carbon monoxide as ligands. Furthermore, the initial incorporation of HDA into the polymer is at least tenfold greater than for any of the other hemin complexes we have studied. This enrichment could be attributed to equilibria found in hemins with two attached bases, which would raise the effective concentration of hemins in the vicinity of a hemin already attached to the polymer chain. According to Momenteau and co-workers,[18] an iron porphyrin with covalent bound axial bases has several potential equilibria:



(4)

In solution other possible interactions exist:



(5)

Thus HDA could exist in aggregates in solution or at the growing end of a polymer chain. Through such equilibria the porphyrin vinyl groups would be held in close proximity to the growing chain end and thus polymerization may be sterically assisted. During purification of the S/HDA·24 sample on the Biobeads SX2 column, we observed that the HDA monomer is completely consumed after 24 h and the copolymer composition is equal to the maximum theoretical hemin enrichment for the yield obtained. This explains the sharp linear decline of hemin enrichment shown in Figure 3. The depression of the yield vs. time curve implies the heme radical on the polymer terminus is less reactive than a styryl radical.

When the imidazolyl ligands of Fe^{II}HDA are replaced by carbon monoxide, the polymerization is very similar to that for HDME·CO. The rate of polymerization is nearly that of pure polystyrene and the polymer HDA content is about the same as found for the other iron porphyrin derivatives studied in this work.

Molecular Weight Studies. Owing to the large number of samples and small yield of polymer for some cases, samples taken at 6 h were selected for molecular weight study. Table IA compares the molecular weight of pure polystyrene to the various ligated iron porphyrin/styrene copolymers synthesized under identical conditions.

The lower molecular weight for copolymer systems than for pure polystyrene could be explained by the presence of chain-transfer agents such as water during ligand addition; however, the polydispersity should be about the same for each case. For S/HDME·$(IM)_2$ the polydispersity is 2 times greater than for the other polymerizations. This supports our hypothesis, presented above, that the Fe^{III}HDME acts as a chain-transfer agent or retarder. As the Fe(III) is reduced to Fe(II) the ligand binds, the chain-transfer agent is consumed, and the molecular weight increases.

We studied the molecular weight of three samples from the S/HDME·CO polymerization to see if there was any change in molecular weight with time and decreasing heme content. The results are given in Table IB. The molecular weight appears to increase very slightly with time with a concurrent increase in the polydispersity index. There is about one heme group per two polymer chains.

It is imperative for our future work to know whether iron porphyrins are incorporated only on the chain terminus, in the middle of a chain, or both. If iron porphyrins are chain terminators one would expect that increasing the monomer feed of HDME would significantly affect the molecular weight. The series of S/HDME·CO polymers of varying heme concentration showed no change in molecular weight with increasing heme concentration (Table II). Thus we can conclude that HDME·CO is incorporated into the polymer backbone. If the feed concentration was increased to a S/HDME ratio of 19.8×10^{-4}, one could expect more than one heme to be incorporated per polymer chain under these experimental conditions.

The molecular weights of the S/HDA·CO copolymers, shown in Table IC, are comparable to those of the other copolymers formed in the presence of six-coordinate iron

porphyrins. However, the S/HDA copolymers show an increase in molecular weight with decreasing HDA feed concentration (increasing reaction time). Earlier samples in the S/HDA copolymerization have a very high weight fraction of HDA in the copolymer and a large number of hemins per chain.

Conclusions

Iron protoporphyrins without strong axial ligands, such as HDME in the Fe(II) and Fe(III) state, appear to retard polymerization through reactions of a radical with the iron atom via redox reactions. The retardation is seen in the very slow rate of conversion for these copolymers in comparison with pure polystyrene. Ligands such as carbon monoxide, cyanide, and 1-methylimidazole prevent the reaction of a radical with the central iron and allow polymerization to proceed in a usual manner. The molecular weight of a heme/styrene copolymer with a carbon monoxide ligand remains constant, despite varying heme concentration, which suggests that heme is not a chain-terminating agent and is incorporated in the polymer chain.

Protoporphyrins are very reactive vinyl monomers owing to the conjugation with the porphyrin ring. This may be seen in the considerable enrichment of iron porphyrin in the polymer composition from the monomer feed. Thus one would expect a relatively slow rate of polymerization. This is seen in the S/HDA case, where the polymer is composed of a significant amount of hemin and the rate of conversion is slower than those polymerizations where the iron porphyrin enrichment is less significant. Also it appears that Fe(III) hemins polymerize more slowly and are more reactive monomers than Fe(II) hemes, possibly due to the greater resonance stabilization of the radical. This is observed in comparing the slower rate of conversion of S/HDME·$(CN)_2$ to those of S/HDME·CO and S/Fe^{II}HDME·$(IM)_2$.

We have postulated a mechanism of hemin enrichment observed in the S/HDA polymerization where the axial basis of the HDA, in solution or at the end of a polymer chain, may bind to nearby hemins. The physical proximity of these monomers results in an increased probability of hemin–hemin polymerization over hemin–styrene copolymerization. We have shown that when one of these ligands is displaced, as in the S/Fe^{II}HDA·CO polymerization, the reaction proceeds as a usual styrene–heme copolymerization.

Registry No. S/Fe^{II}HDME·CO, 85166-72-9; S/Fe^{III}HDME·$(CN)_2^-$, 85166-73-0; S/Fe^{II}HDME·$(IM)_2$, 85185-10-0; S/Fe^{III}HDA, 85166-75-2; S/Fe^{II}HDA·CO, 85166-77-4; S/Fe^{II}HDME, 78035-29-7; S/Fe^{III}HDME, 85166-78-5.

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Energetics of Diacetylene Photopolymerization: A Calorimetric Study

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Received September 23, 1982

ABSTRACT: A detailed calorimetric study is presented for the photopolymerization of a highly radiation-sensitive diacetylene. The polymerization kinetics, heat of polymerization, and quantum yield are presented and compared to photoacoustic studies of the same diacetylene compound. The quantum yield is very high (~125), in good agreement with the photoacoustic results. The heat of polymerization is 0.95 eV per monomer unit, a value that is considerably lower than the value derived from previous thermal polymerization studies of other diacetylenes. We conclude from these results that the energetics of diacetylene solid-state polymerization are influenced by differences in side-group interactions. An unfavorable side-group interaction in the polymer vs. the monomer leads to a decreased heat of polymerization, higher photopolymerization quantum yields, and a high activation energy for thermal polymerization. Favorable polymer side-group interactions are predicted to show the opposite behavior.

I. Introduction

Over the past few years differential scanning calorimetry (DSC) has been used to study basic photoinitiated polymerization phenomena, including polymerization kinetics for various photocurable polymer systems.[1-3] These photocurable systems are mainly used for coatings and printing inks. DSC is especially suited to study photopolymerization kinetics because the rate of the reaction can be measured directly and only small samples are required.

We have utilized the technique of photocalorimetry to study the UV-induced solid-state polymerization of a diacetylene. The solid-state reaction of diacetylenes can be initiated by thermal annealing,[4] pressure, UV,[5] high-energy

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