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Organometallic Polymers. XXVII. Radical-Initiated Polymerization and Copolymerization of π -(2, 4-Hexadien-1-yl Acrylate) tricarbonyliron

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**Organometallic Polymers. XXVII.
Radical-Initiated Polymerization and
Copolymerization of π -(2,4-Hexadien-1-yl
Acrylate)tricarbonyliron**

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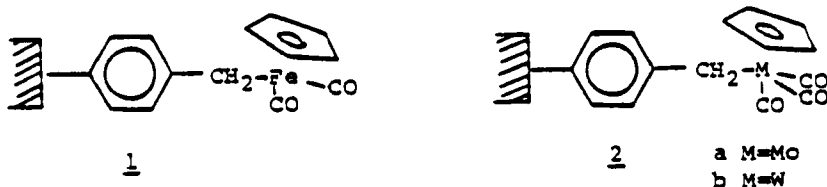
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ABSTRACT

The novel monomer, π -(2,4-hexadiene-1-yl acrylate) tri-carbonyliron (HATI), has been prepared by two routes. It was homopolymerized and copolymerized with acrylonitrile, vinyl acetate, styrene, and methyl acrylate in benzene solutions. In all cases azobisisobutyronitrile was the initiator. The relative reactivity ratios, where HATI is defined as M_1 , were determined: $r_1 = 0.34$, $r_2 = 0.74$, $M_2 =$ acrylonitrile; $r_1 = 2.0$, $r_2 = 0.05$, $M_2 =$ vinyl acetate; $r_1 = 0.26$, $r_2 = 1.81$, $M_2 =$ styrene; and $r_1 = 0.30$, $r_2 = 0.74$, $M_2 =$ methyl acrylate. The homo- and copolymers

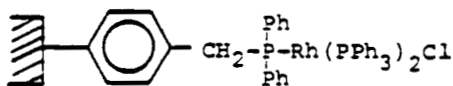
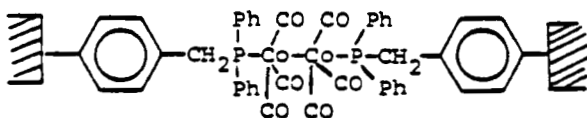
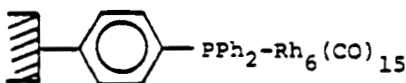
had high values of T_g . When polymerizations are carried out at high concentrations, a very high molecular weight tail is observed in HATI homopolymerizations and in HATI-methyl acrylate copolymerizations. The polymers were characterized by IR, gel permeation chromatography, viscosity, and differential scanning calorimetry studies. Finally, thermal decompositions carried out in air resulted in decomposition of the $\text{Fe}(\text{CO})_3$ group, producing Fe_2O_3 as a fine powder. Thermal decomposition under nitrogen (in solution and on solids ground into KBr pellets) resulted in slow destruction of the $\text{Fe}(\text{CO})_3$ groups but the resulting polymer mass was insoluble, and the question of what form the iron exists in (Fe metal, oxides, carbides, etc.) has not been answered.

In the past few years our group has studied the copolymerization behavior of several vinyl monomers containing transition metal carbonyl moieties. Examples include π -(benzyl acrylate)tricarbonylchromium [1], styrenetricarbonylchromium [2], vinylcyclopentadienyltricarbonylmanganese [3], and π -(2-phenylethyl acrylate)tricarbonylchromium [4]. In addition the synthesis and thermal decomposition of polystyrene-bound metal carbonyls including 1 and 2a and 2b have been completed [5].



Similarly, a series of polymer-bound metal carbonyls, where a phosphorous-metal bond attaches the metal to the polymer backbone, have now appeared from several laboratories [6-8] where they have been used as fixed bed catalysts. Examples include 3 [6], 4 [7], and 5 [8].

Copolymerization studies indicated that vinylcyclopentadienyltricarbonylmanganese was a highly electron-rich vinyl monomer [3] resembling vinylferrocene [9], while styrenetricarbonylchromium could not be characterized as either an electron-rich or an electron-deficient monomer [2, 10]. The reactivity ratios studies performed to date on the acrylates of transition metal-containing substituents (i.e., ferrocenylmethyl [11], ferrocenylethyl [12], π -(benzyl)tricarbonylchromium [1], and π -(2-phenylethyl)tricarbonylchromium [4]) have not fit any consistent pattern other than the observation

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that the r_1 values of ferrocenylmethyl acrylate and methacrylate are very small, probably due to steric factors [12].

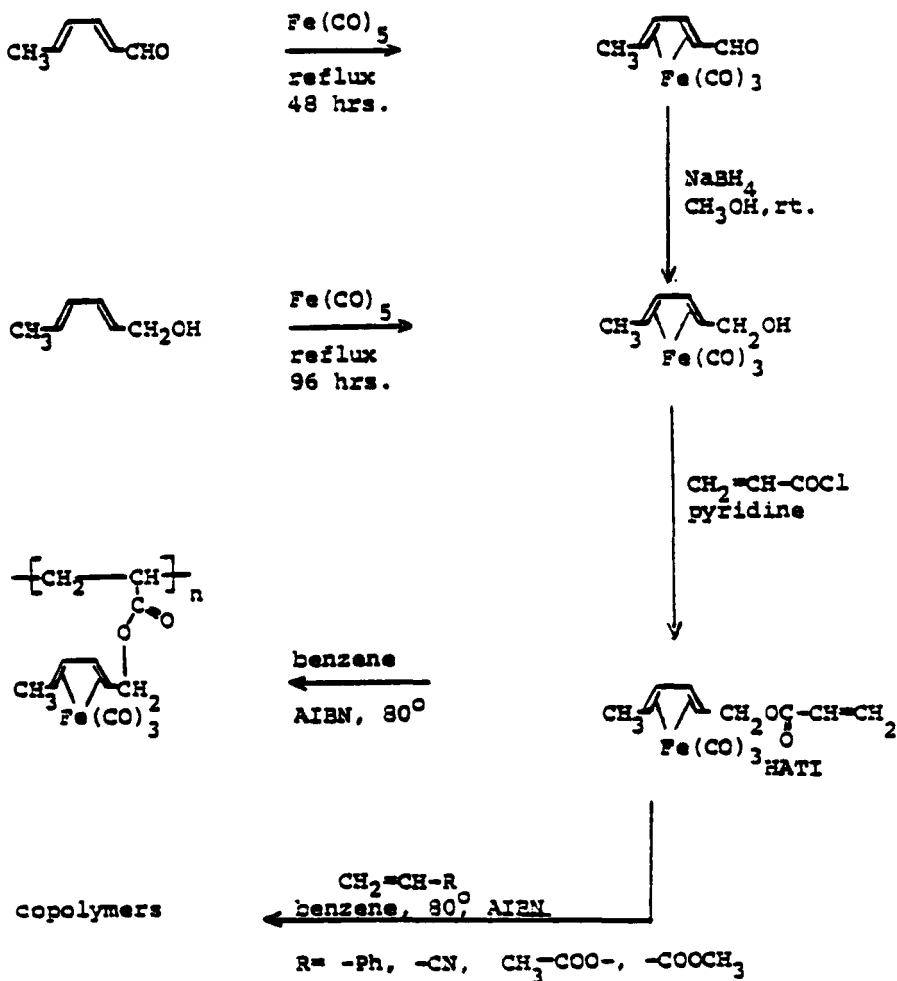
Aside from a few other scattered reports [13-15], polymers containing metal carbonyl functions are rare and no π -(diene)tricarbonyliron monomers have been previously prepared or copolymerized.

RESULTS

Monomer and Polymer Synthesis

The novel acrylate monomer, π -(2,4-hexadiene-1-yl acrylate)tricarbonyliron (HATI), has been synthesized by the two routes shown in Scheme 1. In deoxygenated benzene solutions of HATI were readily homopolymerized or copolymerized with styrene, acrylonitrile, methyl acrylate, or vinyl acetate using azobisisobutyronitrile (AIBN) initiation. All polymerization studies were conducted at 80°C. Each homopolymer or copolymer was purified by repeated reprecipitations from benzene into petroleum ether (30 to 60°C) and drying (in vacuo).

A large series of copolymerizations were carried out in order to establish the reactivity ratios of HATI with styrene, acrylonitrile, methyl acrylate, and vinyl acetate. Representative copolymerizations



SCHEME 1.

are summarized in Tables 1 to 4. The Mortimer-Tidwell method [16, 17], which employs the optimum experimental M_1/M_2 ratios after establishing the approximate r_1 and r_2 values from a series of initial studies, was used. Our use of this technique, employing the integrated form of the copolymer equation, has been extensively described elsewhere [3, 4]. The reactivity ratios are summarized for each monomer pair in footnotes to Tables 1 to 4, and the 95% joint confidence limits for these ratios, defined by Eq. (11) of Ref. 16, are plotted in Fig. 1.

TABLE 1. Copolymerization of π -(2,4-Hexadien-1-yl acrylate)tricarbonyliron (M_1) and Acrylonitrile (M_2) at 80° in Benzene Solution^a

Copolymer No.	M_1 charged (g)	M_2 charged (g)	Mole % M_1 charged	AIBN (g)	Reaction time (hr)	Copolymer yield (%)	Mole % M_1 in copolymer
1 ^b	1.022		35.0	0.0137	6.0	15.3	33.2
2 ^b	1.022		35.0	0.0137	18.0	26.2	32.0
3 ^b	1.022		35.0	0.0137	20.0	27.4	33.4
4 ^b	1.022		35.0	0.0137	12.0	22.5	33.5
5 ^b	1.022		35.0	0.0137	6.0	14.2	33.8
6 ^b	1.898		65.0	0.0208	18.0	22.6	55.0
7 ^b	1.898		65.0	0.0208	24.0	26.4	55.5
8 ^b	1.898		65.0	0.0208	18.0	23.2	54.8
9 ^b	1.898		65.0	0.0208	6.0	18.5	54.9
10 ^b	1.898		65.0	0.0208	2.0	14.1	55.1
11	2.497		85.5	0.0257	1.8	21.7	85.5
12	2.497		85.5	0.0257	2.0	23.5	85.5
13	2.497		85.5	0.0257	1.8	20.5	83.3
14	2.497		85.5	0.0257	1.8	20.4	82.2
15	2.497		85.5	0.0257	1.8	20.3	82.9

^aTen milliliters of benzene used in each run. Reactivity ratios: $r_1 = 0.34$, $r_2 = 0.74$.

^bDesignates runs from which r_1 and r_2 were calculated.

TABLE 2. Copolymerizations of π -(2,4-Hexadien-1-yl Acrylate) tricarbonyliron (M_1) and Vinyl Acetate (M_2) at 80° in Benzene Solution^a

Copolymer No.	M_1 charged (g)	M_2 charged	Mole % M_1 charged	AIBN (g)	Reaction time (hr)	Copolymer yield (%)	Mole % of M_1 in copolymer
1 ^b	1.022		35.0	0.0158	20.0	32.2	62.4
2 ^b	1.022		35.0	0.0158	22.0	33.9	62.6
3 ^b	1.022		35.0	0.0158	3.0	21.5	64.0
4 ^b	1.022		35.0	0.0158	1.0	9.6	65.0
5 ^b	1.022		35.0	0.0158	22.0	33.1	63.0
6	1.898		65.0	0.0220	20.0	39.0	80.1
7	1.898		65.0	0.0220	21.0	40.2	79.9
8	1.898		65.0	0.0220	3.0	26.9	80.1
9	1.898		65.0	0.0220	1.0	12.8	82.1
10	1.898		65.0	0.0220	15.0	31.8	79.9
11	1.489		51.0	0.0191	2.0	24.9	85.7
12	1.489		51.0	0.0191	2.0	25.9	85.3
13	1.489		51.0	0.0191	2.0	25.2	83.9
14	1.489		51.0	0.0191	2.0	24.2	85.6
15	1.489		51.0	0.0191	2.0	24.5	84.6
16 ^b	0.182		2.5	0.0228	2.0	15.0	18.3
17 ^b	0.182		2.5	0.0228	2.0	25.9	8.7
18 ^b	0.182		2.5	0.0228	2.0	25.1	9.4
19 ^b	0.182		2.5	0.0228	1.0	13.6	19.3
20 ^b	0.182		2.5	0.0228	1.0	13.5	18.1

^aTen milliliters of benzene used in each run. Reactivity ratios: $r_1 = 2.0$, $r_2 = 0.05$.

^bDesignates runs from which r_1 and r_2 were calculated.

TABLE 3. Copolymerizations of π -(2,4-Hexadien-1-yl Acrylate)tricarboonyliron (M_1) and Styrene (M_2) at 80° in Benzene Solutions^a

Copolymer No.	M_1 charged (g)	M_1 charged	Mole % M_1 charged	AIBN (g)	Reaction time (hr)	Copolymer yield (%)	Mole % of M_1 in copolymer
1 ^b	1.226		35	0.0204	3.5	15.4	21.8
2 ^b	1.226		35	0.0204	7.0	29.8	22.3
3 ^b	1.226		35	0.0204	14.0	36.3	23.1
4 ^b	1.226		35	0.0204	48.0	53.4	24.5
5 ^b	1.226		35	0.0204	9.0	32.5	23.0
6	1.898		65	0.0226	36.0	49.5	50.4
7	1.898		65	0.0226	14.0	42.8	49.4
8	1.898		65	0.0226	3.5	33.4	47.4
9	1.898		65	0.0226	0.5	4.2	43.1
10	1.898		65	0.0226	1.5	19.4	44.9
11 ^b	2.657		91	0.0275	2.0	22.7	78.7
12 ^b	2.657		91	0.0275	2.0	24.7	81.4
13 ^b	2.657		91	0.0275	2.0	23.5	78.9
14 ^b	2.657		91	0.0275	2.0	22.5	79.4
15 ^b	2.657		91	0.0275	2.0	22.2	80.5

^aTen milliliters of benzene used in each run. Reactivity ratios: $r_1 = 0.26$, $r_2 = 1.81$.

^bDesignates runs from which r_1 and r_2 were calculated.

TABLE 4. Copolymerizations of π -(2,4-Hexadien-1-yl Acrylate)tricarbonyliron (M_1) and Methyl Acrylate (M_2) at 80° in Benzene Solutions^a

Copolymer No.	M_1 charged (g)	M_2 charged (g)	Mole % M_1 charged	AIBN (g)	Reaction time (hr)	Copolymer yield (%)	Mole % of M_1 in copolymer
1 ^b	1.022		35	0.0158	96.0	63.1	33.4
2 ^b	1.022		35	0.0158	15.0	20.1	33.1
3 ^b	1.022		35	0.0158	3.0	8.0	32.7
4 ^b	1.022		35	0.0158	15.0	20.0	33.0
5 ^b	1.022		35	0.0158	65.0	38.2	33.2
6 ^b	1.898		65	0.0220	72.0	27.9	54.1
7 ^b	1.898		65	0.0220	10.0	10.0	52.9
8 ^b	1.898		65	0.0220	2.0	2.7	53.1
9 ^b	1.898		65	0.0220	76.0	29.2	54.4
10	2.541		87	0.0265	2.0	29.7	94.2
11	2.541		87	0.0265	1.5	24.0	89.8
12	2.541		87	0.0265	1.5	26.2	89.1
13	2.541		87	0.0265	1.5	25.0	91.6
14	2.541		87	0.0265	1.5	26.4	90.4

^aTen milliliters of benzene used in each run. Reactivity ratios: $r_1 = 0.30$, $r_2 = 0.74$.

^bDesignates runs from which r_1 and r_2 were calculated.

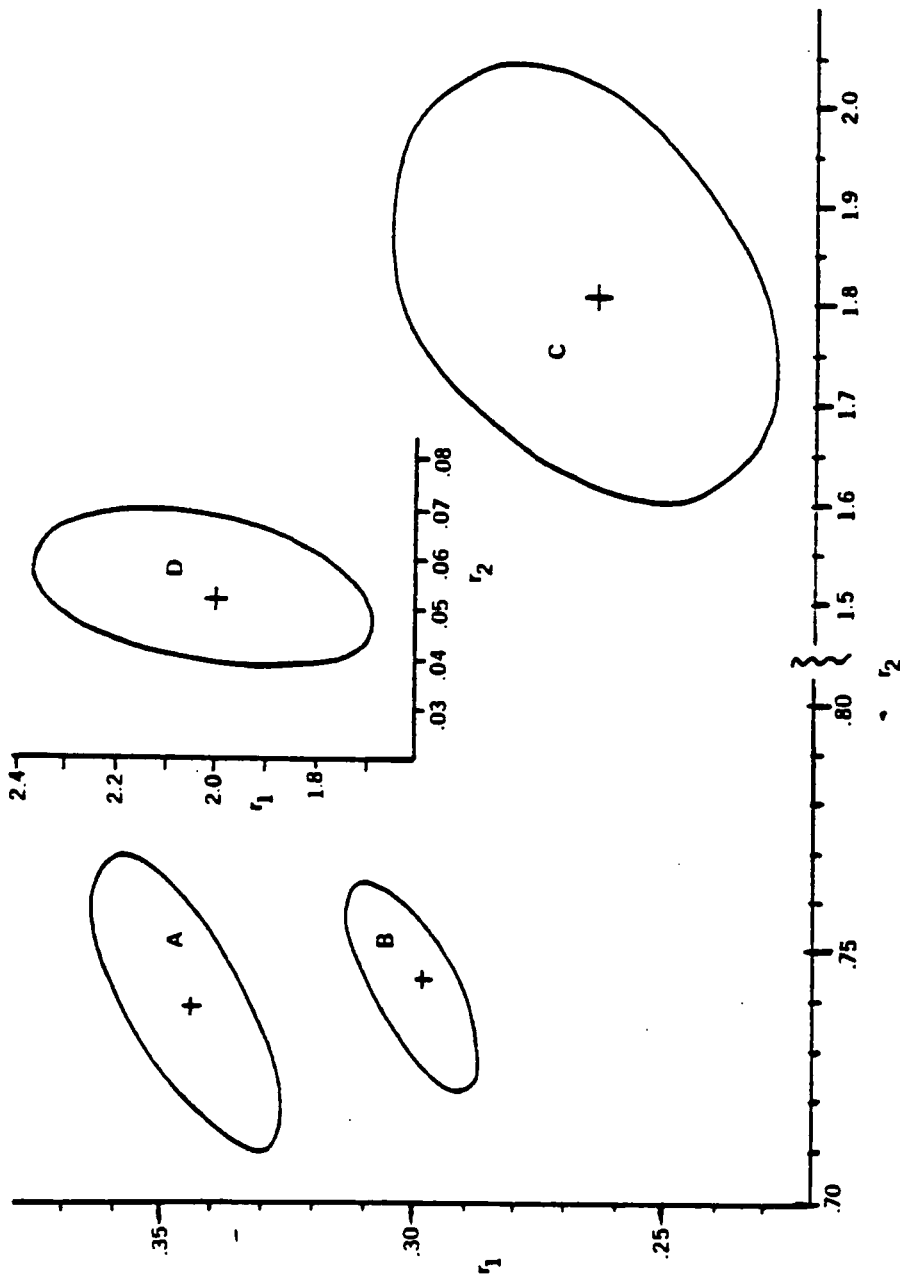


FIG. 1. Approximate 95% joint confidence limits of r_1 and r_2 for copolymerizations of π -(2,4-hexadiene-1-yl acrylate) with (A) acrylonitrile, (B) methyl acrylate, (C) styrene, and (D) vinyl acetate.

The reactivity ratios were obtained with rather small confidence limits, and these values were then successfully tested by running composition-conversion tests in regions where the M_1^2/M_2^2 ratio was not optimized. Thus these ratios are considered reliable. Q-e [18] maps of all four copolymerizations were studied, but no values of Q or e could be assigned to HATI which were consistent for all the copolymerizations. Thus it must be concluded the Q-e scheme cannot be applied (at least under the conditions used here) to HATI. There is also no orderly deviation in HATI's e value in order of increasing electron demand from M_2 going from styrene to acrylonitrile. This suggests that there is no systematic deviation from a terminal mechanism to another pathway (such as increasing contribution from a charge-transfer mechanism [19]). Without any other information, steric effects can be suggested to account for this deviation from the Q-e scheme.

The homopolymerization of HATI in benzene at 80°C was carried out using 1 wt% of AIBN. In solutions where the monomer concentration ranged from 1.5 to 4 g/10 ml benzene, the yields were 20 to 30% after 24 hr. The values of \bar{M}_n and \bar{M}_w were characteristically 9,000 to 10,000 and 17,000 to 19,000, respectively. Upon using 0.05 wt% of AIBN initially, and a like amount 4 hr later, it was possible to obtain polymer yields of 50% or greater. A high molecular weight tail (as high as 1.6×10^5) showed some branching was occurring in these runs, but in 20 hr no gel formation was noted. Gel formation was pronounced in methyl acrylate-HATI copolymers where the HATI/methyl acrylate ratio was low, but as more HATI was added, gel formation was no longer found (see Entries 7 and 8 in Table 5).

Characterization and Thermal Decomposition

The molecular weights and viscosities for a representative series of polymers are listed in Table 5. Table 5 also lists values of T_g as determined from differential scanning calorimetry (DSC) studies. HATI had the effect of sharply increasing T_g values of these copolymers. This property has previously been noticed for the ferrocene nucleus, both in the vinylferrocene [20] and ferrocenyl acrylate copolymers [20], and with π -complexed $\text{Cr}(\text{CO})_3$ -containing polymers [1, 4]. The T_g value of the HATI homopolymer could not be established by DSC. Both high and low molecular weight fractions exhibited a small exotherm at 174°C followed by a large exotherm at 194°C. The values of T_g for the copolymers could not be fitted to the Fox equation [21]

$$\left(\frac{1}{T_g} = \frac{W_1}{T_g(1)} + \frac{W_2}{T_g(2)} \right)$$

TABLE 5. Molecular Weight and Intrinsic Viscosity Determinations for a Representative Series of Copolymers of HATI (M_1)

Copolymer No. ^a	Mole % M_1 in Copolymer	$[\eta]^b$ (dl/g)	\bar{M}_n^c	\bar{M}_w^c	\bar{M}_w/\bar{M}_n	T_g ($^{\circ}\text{C}$) ^d
HATI-AN-3	33.4	0.054	2,600	5,260	2.00	125
HATI-AN-11	85.5	0.070	7,100	19,700	2.80	158
HATI-VA-11	85.7	0.057	11,200	27,400	2.46	
HATI-VA-19	19.3	0.148	9,800	46,100	4.72	
HATI-Styrene-2	22.3	0.098	8,800	22,600	2.57	153
HATI-Styrene-12	81.4	0.100	9,300	28,000	3.01	174
HATI-MA-1e	33.4	0.177	8,000	4×10^6		165
HATI-MA-14	90.4	0.080	8,800	24,500	2.80	178
HATI-1	100	0.080	8,600	13×10^5		
HATI-2	100	0.060	9,300	17,800	1.91	

^aCopolymer numbers refer to those in Tables 1-4 and HATI = π -(2,4-hexadien-1-yl acrylate)triacrylonitrile, AN = acrylonitrile, VA = vinyl acetate, and MA = methyl acrylate.

^bDetermined in tetrahydrofuran at 30 $^{\circ}\text{C}$.

^cDetermined by gel permeation chromatography using the universal calibration technique.

^dObtained by differential scanning calorimetry. The copolymers HATI-VA-11 and HATI-VA-19 underwent exothermic reactions at 199 and 216 $^{\circ}\text{C}$, respectively.

^eLong, broad, high, molecular weight tail due to some cross-linking (trace of gel formation noted).

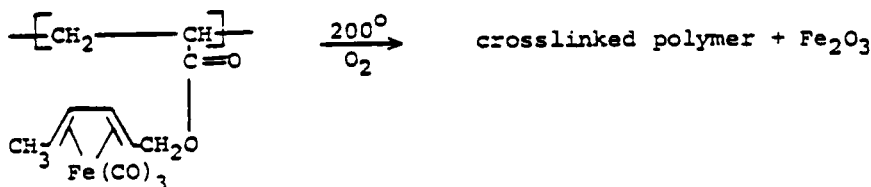
(if the relation had held, one could have calculated T_g for HATI) but the general trend predicted by the equation was seen. The deviation noted is not unexpected since the molecular weights of the copolymer samples within a series varied, and T_g is known to depend on molecular weight [21, 22].

Organic polymers containing π -dienetricarbonyliron functions are of particular interest because their thermal decomposition could free either iron or iron oxide within the polymer. One can picture the application of such a decomposition to the synthesis of a "solution of metal or metal oxide" within the polymer mass. Currently, mixing metal oxides into polymers results only in heterogeneous composite materials since the particle size of the metal oxides cannot be infinitely reduced. A complimentary method to generate metal oxide particles that are homogeneously dispersed at the molecular level is needed. Thus a series of thermal decomposition studies were performed on HATI homo- and copolymers, both neat and in solution. The copolymers studied were HATI-acrylonitrile-3 and HATI-styrene-2. Thermal decompositions were carried out both in air and under nitrogen, in cumene solutions, on polymer samples held in KBr pellets, and on neat bulk samples. Since a large DSC exotherm at 194°C had been noted, the decompositions were carried out from 190 to 200°C.

When soluble poly(HATI) and the soluble copolymers listed above were heated in glass sample tubes for 15 min in the presence of air, the deposition of red ferric oxide (Fe_2O_3) was noted on the sides of the tube. The resulting polymers became black and were insoluble in organic solvents (acetone, THF, benzene, ethyl acetate). The body of the now cross-linked polymer also contained Fe_2O_3 . The mechanism of cross-linking is not known but reactions at the diene unit, oxidative cross-linking along the backbone, and the depolymerization-repolymerization sequences are all possible.

The thermal decompositions were followed by IR. KBr pellets containing the polymer to be studied were alternately heated and then cooled (at 10 min intervals). A steady disappearance of the iron-bound carbonyls was noted, but the pellets also became dark black and the quality of the spectra decreased with increasing decomposition. After only 10 min the acrylonitrile copolymers were largely decomposed. A single cross-linked styrene-divinylbenzene-HATI terpolymer resin was made (3 mole % HATI). This was decomposed and the Fe_2O_3 formed remained in the body of the resin.

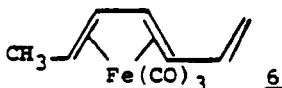
Thermal decompositions, conducted under nitrogen, gave no evidence of Fe_2O_3 formation on the sides of the glass tube. No metallic mirror was found. The IR spectra showed a steady decrease in the carbonyl intensities and CO was evolved. While the carbonyl bands disappeared more slowly, the final result was the formation of insoluble polymeric decomposition products with poor quality IR spectra. After long heating periods (30 to 60 min), a significant number of π -dienetricarbonyliron



groups remained intact (IR). The chemical nature of the iron in these decomposition products is not known. Any attempts to decompose the resulting polymeric mass to isolate the iron could change the chemical form in which it is present.

In an attempt to reduce the cross-linking process, thermal decompositions were performed on degassed cumene solutions under purified nitrogen. This approach did not succeed. The solutions were heated from 130 to 190°C over a 30-min period. After a 30-min heating period all the tubes contained a dark brown insoluble polymer precipitate, and solid insoluble polymer films were deposited on the sides of the tube. There was no evidence of any free iron, and the resulting precipitates still contained π -dienetricarbonyliron groups (IR). The recovered cross-linked polymer was brittle, had no elastomeric properties, and was insoluble in organic solvents. The chemical state of iron within the cross-linked polymers resulting from decomposition in both air and N_2 is currently under investigation using both Mössbauer spectroscopy and ESCA techniques [23].

The ready homo- and copolymerizability of HATI stands in marked contrast to that of its vinyl analog, **6**. Monomer **6** has resisted several initial homopolymerization and copolymerization (with styrene) attempts in benzene solution using radicals initiators [24].



EXPERIMENTAL SECTION

Synthesis of π -(2,4-Hexadien-1-ol)tricarbonyliron

A. A solution of 2,4-hexadien-1-ol (67.5 g, 0.69 mole) and penta-carbonyliron (160 g, 0.82 mole) was refluxed under nitrogen for 96 hr. The volatile products were removed under reduced pressure and crude π -(2,4-hexadien-1-ol)tricarbonyliron was distilled and purified by redistillation (96 to 97°C, 0.3 mm) to give 35 g (0.15 mole). The

complex solidified on refrigeration and was recrystallized from 30 to 60°C petroleum ether to afford yellow needles, mp 37° (Ref. 26, 37°C).

Analysis: Calculated: C, 45.41; H, 4.23; Fe, 23.46. Found: C, 45.71; H, 4.42; Fe, 23.10.

B. A solution of freshly distilled 2,4-hexadien-1-ol (55 g, 0.57 mole) and pentacarbonyliron (225 g, 1.15 moles) was refluxed 48 hr under nitrogen. The solution was cooled and the volatile products were removed under reduced pressure, followed by vacuum distillation of the residual oil which gave π -(2,4-hexadien-1-ol)tricarbonyliron (62.5 g, 2.66 moles) bp 102 to 104°C at 1.0 mm (Ref. 25, 112°C/1.3 mm). To a stirred methanol (250 ml) solution of π -(2,4-hexadien-1-ol)tricarbonyliron (39.3 g, 0.166 mole), sodium borohydride (3.0 g, 0.079 mole) was added. The reaction temperature was maintained at 25 to 30°C during the addition and then stirred an additional 30 min at this temperature. The reaction was hydrolyzed with distilled water (200 ml) and the product was extracted with three portions (150 ml each) of ether. The combined extract was water washed and dried (MgSO_4). The solvent was removed to give 37.5 g (0.15 mole) of crude alcohol which was purified by recrystallization from 30 to 60°C petroleum ether to give the title compound (mp 37°) which was identical to that prepared by Route A.

π -(2,4-Hexadien-1-yl acrylate)tricarbonyliron

Dry pyridine (14 ml) and π -(2,4-hexadien-1-ol)tricarbonyliron (19.04 g, 0.08 mole) were added to anhydrous ethyl ether (600 ml) and the solution was flushed with nitrogen. After cooling to 0°C a solution of acrylyl chloride (14.0 ml, 0.176 mole) in ether (50 ml) was added dropwise over a 30-min period with stirring. Reaction was immediate as evidenced by the precipitation of pyridine hydrochloride. The reaction was warmed to 25°C and stirring continued for 1 hr. The reaction was diluted with 200 ml of ether and filtered to remove the pyridine hydrochloride. The pyridine hydrochloride was thoroughly washed twice with 100 ml portions of ether. The combined ether layers were washed three times with 300 ml portions of saturated aqueous NaHCO_3 and twice with 300 ml portions of distilled water. After drying (MgSO_4), filtering, and evaporation of ether, the crude acrylate was isolated (17.0 g). It was purified by chromatography (60-200 mesh silica gel with benzene as elutant). After removal of benzene under high vacuum, the purified acrylate (15 g, 0.05 mole) was obtained NMR pure as a brown liquid: IR (film) 3040, 2960, 2920, 2860, 2050, 1985-1945, 1720, 1630, 1612, 1440, 1400, 1375, 1290, 1260, 1180, 1050, 1035, 980, 960, 805, 875, 860, and 620 cm^{-1} ; NMR (CCl_4), δ , 1.39 (d, 3H, CH_3), 4.10 (d, 2H, CH_2O), 6.48-5.10 (complex multiplet, ABX, vinyl superimposed in part on π -diene protons), 4.80-5.30 (m, 2H, diene protons at C-3 and C-4), 0.9 to 1.38 (m, 2H, diene protons at C-2 and C-5).

Analysis: Calculated: C, 49.35 H, 4.14; Fe, 19.12. Found: C, 49.10, H, 4.00; Fe, 18.90.

Polymerizations and Polymer Characterizations

All comonomers were purchased and purified conventionally before use. The π -(2,4-hexadien-1-yl acrylate)tricarbonyliron was prepared and purified (as above) shortly before use. All polymerizations were carried out in Fischer-Porter aerosol compatibility tubes in benzene at 80°C using twice recrystallized AIBN as the initiator. In each case the reaction mixture was triply gassed using the freeze-thaw technique and repressurized with pure nitrogen. The polymers were purified by three reprecipitations in 30 to 60°C petroleum ether and dried in a vacuum oven (50 to 60°C) for 24 hr at 1 to 2 mm. Copolymer compositions were determined by elemental analyses. The primary technique employed for iron determinations was x-ray fluorescence, and every fifth sample was checked by atomic absorption. Several samples were also checked gravimetrically. Viscosity measurements were made in THF at 30°C using Cannon-Ubbelohde viscometers. Gel permeation chromatograms were obtained at the same temperature in THF on a Waters Model 301 instrument. The Universal calibration technique [26] was then employed for molecular weight calculations. A Perkin Elmer Model 1B differential scanning calorimeter was employed using a 10°C/min heating rate. The IR spectra were obtained (in KBr) using a Perkin Elmer Model 521 spectrometer. The characteristic bands for the purified polymers are summarized below.

HATI-Acrylonitrile Copolymer: 3020, 2960-2920, 2860, 2050, 1985-1940, 1720, 1440, 1375, 1250, 1150, 1025, 920, and 620 cm^{-1} .

HATI-Vinyl Acetate Copolymer: 3020, 2960, 2930, 2860, 2050, 1985-1940, 1720, 1437, 1375, 1230, 1150, 1020, 920, and 620 cm^{-1} .

HATI-Styrene Copolymer: 3030, 2960-2930, 2870, 2050, 1985-1940, 1720, 1485, 1440, 1375, 1250, 1145, 1025, 920, 835, 755, 695, and 620 cm^{-1} .

HATI-Methyl Acrylate Copolymer: 3020, 2950, 2930, 2860, 2050, 1985-1940, 1720, 1480, 1435, 1372, 1315, 1235, 1145, 1020, 920, 830, 750, 695, and 615 cm^{-1} .

HATI Homopolymer: 3020, 2950, 2930, 2860, 2050, 1985-1940, 1720, 1440, 1375, 1250, 1150, 1025, 920, 835, 750, and 620 cm^{-1} .

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