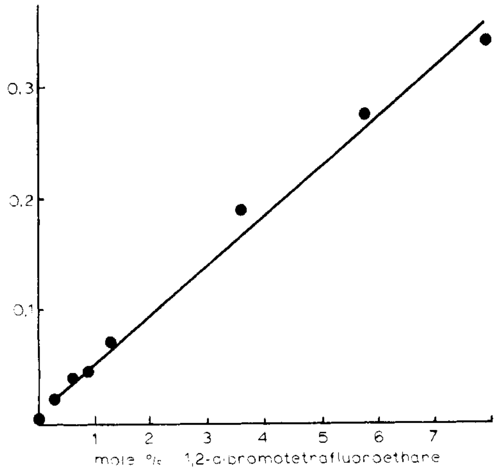

Figure 1. Dependence of polymer floc production on the mole percent of 1,2-dibromotetrafluoroethane. Results are average values from two or more experiments run with 300 mm partial pressure of TFE and a 20 min irradiation time. (Mole percent of initiator is calculated relative to total initiator and monomer.)

in the uv below 270 nm[14] and would be expected to undergo photodissociation of the carbon–bromine bond under irradiation.[8] The presence of air in the reaction chamber did not inhibit the reaction.

Wilkus and Wright[11a] report that the polymer floc produced in the direct irradiation of TFE showed considerable infrared absorption at 980 cm^{-1} due to the presence of either CF_3 groups or cyclic fluorocarbons. In this respect, their product differed from the linear form of poly(tetrafluoroethylene). The polymer floc that was produced when 1,2-dibromotetrafluoroethane was used as initiator showed no infrared absorption near 980 cm^{-1} and was identical with the published spectrum of linear poly(TFE)[11a] and with a spectrum of a sample of linear poly(TFE) powder.[15]

Analysis by mass spectroscopy of the gas phase during and after the 1,2-dibromotetrafluoroethane initiated photopolymerization showed no detectable amounts of cyclic fluorocarbons or other low molecular weight side products. This result is in contrast to the side products reported using other initiators or no initiator.[16]

The polymer floc produced in these reactions contained about 6% bromine by elemental analysis. After heating the floc at 60° under reduced pressure for 12 hr, the amount of bromine present was found to be less than 1.5%, and the carbon and fluorine analyses were 22.87 and 75.72%, respectively (Calcd for poly(TFE): C, 24.0; F, 76.0). Upon heating in air, the floc was found to fuse to a clear film above 200°, and after heating to 320° there was a 10% loss in material noted.

Other halocarbons were tested as initiators in this reaction: carbon tetrachloride, iodomethane, bromoethane, iodoethane, bromotrifluoromethane, and pentafluoroiodoethane. All of these materials did act as initiators, but the products were oils and no polymer floc was produced with any of these compounds. The introduction of bromine, which reacts rapidly with TFE to produce 1,2-dibromotetrafluoroethane, gave results which were identical with experiments using equal molar amounts of 1,2-dibromotetrafluoroethane. Direct gas phase photolysis of 1,2-dibromotetrafluoroethane in the absence of TFE gives a small amount of oily product, but no floc is formed.

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Polymerization of Methyl Methacrylate with *tert*-Butyl Hydroperoxide and Metal Acetylacetonates

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The decomposition of hydroperoxides catalyzed by metal salts and complexes has been extensively studied.[1-3] Several of these studies have used metal acetylacetonates.[2,4-8] In the present work, the effect of a small concentration of acetylacetonates on *tert*-butyl hydroperoxide initiated polymerization of methyl methacrylate in 1-chlorooctane medium has been investigated. To relate this work to that of Osawa et al.,[8] Co(II), Co(III), and Cu(II) catalyzed polymerizations have also been studied in benzene. The decompositon of *tert*-butyl hydroperoxide catalyzed by Co(II) and Co(III) acetylacetonates has been studied in the absence of the monomer as well, in both benzene and 1-chlorooctane media.

Experimental Section

Chemicals. Methyl methacrylate (Eastman Organic Chemicals) was treated with anhydrous Na_2SO_4 and distilled under vacuum. *tert*-Butyl hydroperoxide, Wallace and Tiernan, Inc. (Lucidol Division), was purified by distilling away lower boiling impurities (>95% by iodometric titration). 1-Chlorooctane (Aldrich Chemicals, Inc.) was distilled and its purity checked by gas chromatography. Metal acetylacetonates, McKenzie Chemical Corp., were recrystallized from chloroform, and their purity was ascertained from uv spectra. Spectroanalyzed benzene (Fisher Scientific Co.) was used without purification.

Kinetics. The reactions were performed using either of two techniques. In one, reactants introduced into Carius tubes were frozen at liquid nitrogen temperatures, evacuated, and degassed through three freeze–thaw cycles, sealed under vacuum, and thermostated. Alternately, reactants were saturated with nitrogen, mixed in a thermostated jacketed reactor under a nitrogen atmosphere, and aliquots taken. Rates of polymerization were measured by gravimetric determination of polymer precipitated with methanol. Hydroperoxide was determined by iodometric titration[9] using 0.01 *N* thiosulfate. At very low and at very high percent decomposition of hydroperoxide only an upper or lower limit could be determined. Number average molecular weights, $\bar{M}_n$, were determined viscometrically, using the relation[10]

$$[\eta] = 7.24 \times 10^{-5} \bar{M}_n{}^{0.76}$$

where $[\eta]$ is the intrinsic viscosity. Viscosities were measured at 30° in benzene.

Table I
Methyl Methacrylate Polymerization and *tert*-Butyl Hydroperoxide Decomposition in 1-Chlorooctane (Methyl Methacrylate = 4.16 *M*, *t*-BHP = 0.022 *M*, $M(acac)_n = 1.8 \times 10^{-4}$ *M*)

Metal acetylacetonate	Temperature = 40°							Temperature = 60°							Temperature = 80°						
	Time, hr	*t*-BHP dec, %	$R_d \times 10^7$, mol l.$^{-1}$ sec^{-1}	Conversion, %	$R_p \times 10^5$, mol l.$^{-1}$ sec^{-1}	$\bar{M}_n \times 10^{-5}$	f	Time, hr	*t*-BHP dec, %	$R_d \times 10^7$, mol l.$^{-1}$ sec^{-1}	Conversion, %	$R_p \times 10^5$, mol l.$^{-1}$ sec^{-1}	$\bar{M}_n \times 10^{-5}$	f	Time, hr	*t*-BHP dec, %	$R_d \times 10^7$, mol l.$^{-1}$ sec^{-1}	Conversion, %	$R_p \times 10^5$, mol l.$^{-1}$ sec^{-1}	$\bar{M}_n \times 10^{-5}$	f
None	8	<5		2.2	0.32	2.98		2.5	<5		4.0	1.8	2.98		0.75	<5	1.9	6.4	9.7	2.31	
	12	<5		3.3		3.31		3.5	<5		5.1		2.70		1.17	<5		9.9		2.39	
	15	<5		4.1		3.37		4.5	<5		7.1		2.85		1.5	5.2		13		2.32	0.2
Co(II)	5	16	2.1		0.22			1.0	20	14		1.2			0.22	20	61		3.8		
	8	22		1.1				2.0	30		1.5				0.58	44		1.1			
	12	25		2.0				3.0	35		2.5		0.482	0.028	1.08	54		2.4		0.414	0.021
	15	32		2.8		0.634	0.026	4.5	40		4.7		0.551	0.040	1.5	59		4.2		0.427	0.031
															2.0	62		5.7		0.474	0.037
Co(III)	8	5.5	0.38	2.1	0.29	1.85	0.039	1.0	<5	2.6		1.8			0.5	10	13	4.5	9.2	0.961	0.089
	15	9.0		3.8		1.92	0.042	2.0	7.8		2.9		1.28	0.055	1.08	16		8.4		1.08	0.092
								3.0	12		4.6		1.35	0.054	1.5	21		12		1.16	0.093
								4.5	18		6.8		1.41	0.051							
Mn(II)	8	<5		1.9	0.29			2.5	<5		4.1	1.8			0.75	<5	2.0	6.7	9.5	1.75	
	12	<5		3.0		2.67		4.0	<5		6.3		2.14		1.25	<5		10		1.75	
	15	<5		3.8		2.65		5.0	<5		7.5		2.35		1.75	6.4		14		1.82	0.22
Mn(III)	8	7.7	0.61	2.4	0.35	0.922	0.064	2.5	12	3.1	3.9	1.9	0.668	0.093	0.75	17	15	6.4	9.2	0.466	0.15
	12	10		3.7		0.983	0.071	4.0	18		6.6		0.779	0.089	1.25	26		10		0.458	0.16
	15	11		4.5		1.10	0.070	5.0	21		8.3		0.872	0.086	1.75	35		14		0.483	0.16
Cu(II)	0.33	52	140		1.6			0.08	45	440		6.0			0.08	90	1700		15.3		
	1.0	76						0.17	74						0.17	95		3.3			
	1.5	84		1.3				0.33	80		1.1				0.45	94		6.1		1.04	0.011
	2.5	88		2.7		0.234	0.025	0.83	86		4.6		0.438	0.023	0.58	95		7.4		1.69	0.0087
	3.5	92		4.5		0.452	0.021	1.25	92		6.5		0.895	0.015	0.083	95		11		2.62	0.0084
	4.5	94		6.4		0.626	0.021	1.67	95		8.5		1.12	0.015							
Cr(III)	8	<5		2.0	0.31	2.48		2.5	<5		3.9	1.9	1.65		1.0	<5	2.0	8.4	9.9	1.35	
	15	<5		4.0		2.71		3.5	<5		5.6		1.69		1.5	5.4		13		1.57	0.29
								4.5	<5		7.7		1.87								
Al(III)	15	<5		4.0	0.31	3.12		4.5	<5		7.2	1.9	2.52		1.5	5.9	2.2	12	9.2	1.92	0.20
Ni(II)	15	<5		3.8	0.29	3.06		4.5	<5		7.5	1.9	2.38		1.5	5.7	2.0	12	9.5	2.13	0.19

Table II: Methyl Methacrylate Polymerization and *tert*-Butyl Hydroperoxide Decomposition in Benzene (Methyl Methacrylate = 4.16 *M*, *t*-BHP = 0.022 *M*, M(acac)$_n$ = 1.8 × 10^{-4} *M*)

	Temperature = 40°							Temperature = 60°							Temperature = 80°						
Metal acetyl-aceto-nate	Time, hr	*t*-BHP dec, %	R_d × 10^7, mol l.$^{-1}$ sec^{-1}	Con-ver-sion, %	R_p × 10^5, mol l.$^{-1}$ sec^{-1}	$\overline{M}_n$ × 10^{-5}	f	Time, hr	*t*-BHP dec, %	R_d × 10^7, mol l.$^{-1}$ sec^{-1}	Con-ver-sion, %	R_p × 10^5, mol l^{-1} sec^{-1}	$\overline{M}_n$ × 10^{-5}	f	Time, hr	*t*-BHP dec, %	R_d × 10^7, mol l.$^{-1}$ sec^{-1}	Con-ver-sion, %	R_p × 10^5, mol l.$^{-1}$ sec^{-1}	$\overline{M}_n$ × 10^{-5}	f
None	8	<5		0.60	0.10			2.0	<5		1.2	0.70			0.75	<5		2.2	3.7		
	12	<5		1.1		14.5		3.5	<5		1.8		8.78		1.25	<5		4.3		5.87	
	15	<5		1.3		14.3		4.5	<5		2.7		9.07		1.75	<5		5.7		6.08	
Co(III)	5	<5		0.64	0.15			2.0	<5		1.4	0.82			0.75	<5	2.1	2.3	3.5		
	10	<5		1.4				3.0	<5		2.0				1.25	<5		3.8			
	15	<5		2.0		3.68		3.75	<5		2.7				1.75	5.8		5.3		2.30	0.075
								4.5	<5		3.4		2.88								
Co(II)	5	31	4.5		0.042			0.75	30	29		0.17			0.17	20	82		1.2		
	10	45						1.5	52						0.33	38					
	15	52		0.40				3.0	65		0.38				0.67	55					
	20	57		0.72		0.654	0.0036	4.5	72		0.65		0.519	0.0033	1.0	60		0.85			
															1.75	66		1.84		0.476	0.011
Cu(II)	10	<5		1.5	0.18	2.15		3.0	<5	0.78	3.7	1.2	1.55		1.0	5.3	3.3	4.3	5.0	0.814	0.19
	15	<5		2.3		2.33		4.5	5.6		4.5		1.69	0.14	1.5	7.3		6.5		0.895	0.19

Table III: *tert*-Butyl Hydroperoxide Decomposition (*t*-BHP = 0.022 *M*, M(acac)$_n$ = 1.8 × 10^{-4} *M*)

		Temperature = 40°			Temperature = 60°			Temperature = 80°		
Metal acetyl-acetonate	Solvent	Time, min	*t*-BHP dec, %	R_d × 10^7, mol l.$^{-1}$ sec^{-1}	Time, min	*t*-BHP dec, %	R_d × 10^7, mol l.$^{-1}$ sec^{-1}	Time, min	*t*-BHP dec, %	R_d × 10^7, mol l.$^{-1}$ sec^{-1}
Co(II)	*a*	60	25	17.6	10	33	147	5	49	494
		180	48		30	43		10	78	
		360	60		60	50		30	92	
Co(III)	*a*	300	25	3.52	45	23	21.3	15	33	97.9
		480	35		90	40		60	77	
Co(II)	*b*	60	46	37.7	6	44	354	5	74	988
		180	80		10	62		10	87	
		300	85		20	76		30	95	
					40	86				
					60	90				
					100	95				
Co(III)	*b*	900	5.2	0.218	90	<5		80	<5	
					180	5.2	0.645	130	5.2	1.33

[a] 1-Chlorooctane. [b] Benzene, R_d = rate of hydroperoxide decomposition.

Results and Discussion

In the polymerization of methyl methacrylate in 1-chlorooctane initiated by *tert*-butyl hydroperoxide (*t*-BHP) in the presence of several metal acetylacetonates, [M(acac)$_n$], as well as in their absence, conversion of monomer and hydroperoxide decomposition were measured at 40, 60, and 80° as a function of time. The results are shown in Table I along with the rates of polymerization (R_p) and *t*-BHP decomposition (R_d). The variation of the number average molecular weight, $\bar{M}_n$, of the polymer, and the initiator efficiency, f, with the progress of reaction, are also shown. Cu(II) and Co(II) catalyze the *t*-BHP decomposition most effectively, Mn(III) and Co(III) show intermediate activity, and Al(III), Ni(II), Cr(III), and Mn(II) do not significantly affect the decomposition. That Cu(II) salts catalyze hydroperoxide decomposition has long been known.[11,12,13c] Although in the early stage of the reaction hydroperoxide decomposition seems to follow a first-order pattern, retardation sets in as the reaction progresses. This may be due to the deactivation of the metal by the decomposition products which may block[13] the active sites on the metal and prevent the formation of metal–hydroperoxide complex.[13–17] Hydroperoxide decomposition could also slow down if peroxy radicals abstract hydrogen atoms to reform hydroperoxide molecules. A third possibility is the so-called "complexation" of hydroperoxide[18] with products of decomposition.

A decrease in the rate of hydroperoxide decomposition with the progress of the reaction would result in a decreasing rate of initiation in accord with the observed increase in the molecular weight of the polymer with reaction time at a given temperature. In the Cu(II) catalyzed system in 1-chlorooctane, however, the molecular weight is seen to increase with temperature, apparently owing to rapid depletion of *t*-BHP in the early stage of the reaction. The presence of metal complexes generally tends to lower the molecular weight of the polymer formed due to an increased rate of initiation, as well as chain transfer to the metal ligands. Work in this laboratory has shown that several of the metal acetylacetonates have significant chain transfer constants.[19]

Most of the metal acetylacetonates studied do not significantly affect the rate of polymerization in 1-chlorooctane. However, Cu(acac)$_2$ which best catalyzes hydroperoxide decomposition also catalyzes polymerization. The activation energy for the polymerization in the presence of Cu(acac)$_2$ is seen to be 12.1 kcal/mol as compared with 19.5 kcal/mol in its absence. But, a metal complex which facilitates hydroperoxide decomposition need not catalyze polymerization. Thus, in the Co(II) acetylacetonate system, although peroxide decomposition is enhanced in the presence of the metal, polymerization is actually less than in its absence.

Osawa et al.[8b] have studied the *t*-BHP catalyzed polymerization of methyl methacrylate in the presence of Co(II) and Co(III) acetylacetonates in benzene at metal concentrations ~15 times higher than those used in the present work. It was reported that Co(II) had a measurable catalytic effect on the polymerization rate whereas Co(III) had very little effect. A comparison of these results to ours obtained in 1-chlorooctane suggests that the effectiveness of the metal species may be concentration dependent and sensitive to solvent. To explore this possibility, the Co(II) and Co(III) catalyzed systems were studied in benzene. In an earlier work of Osawa et al.[8a] it was seen that in benzene Cu(II) had a much smaller effect on *t*-BHP decomposition than Co(II) and Co(III) acetylacetonates, whereas in 1-chlorooctane Cu(II) is the most effective catalyst. To confirm this medium effect the Cu(II) catalyzed polymerization was also carried out in benzene. The results of these experiments in benzene are shown in Table II. It is indeed observed that the catalytic effect of Cu(acac)$_2$ on t-BHP decomposition also decreased to such an extent that it is barely noticeable at 80°, and not at all at the lower temperatures. Co(II) catalyzes *t*-BHP decomposition and retards methyl methacrylate polymerization, as in 1-chlorooctane. It may be safely concluded that catalyst activity is solvent sensitive as well as concentration dependent.

A comparison of the polymerization data obtained in the absence of metal in the two solvents indicates a substantially smaller rate in the aromatic solvent. A decrease in autoxidation rates in aromatic solvents has been observed earlier[5b] and attributed to possible formation of phenols.[5b,20] Another factor which could contribute to the decrease in polymerization and autoxidation rates is stabiliza-

Table IV
Activation Parameters

Metal acetyl- acetonate	Solvent	E_d, kcal mol^{-1}	$A_d \times 10^{-5}$	$(E_a)_{calcd}$, kcal mol^{-1}	$(E_a)_{obsd}$, kcal mol^{-1}	$A \times 10^{-6}$
None	*a*	(39.0)^d		24.2	19.5	97.9
Cu(II)	*a*	11.8	0.0209	10.6	12.1	0.00435
Al(III)	*a*				19.2	58.3
Cr(III)	*a*				19.6	112
Ni(II)	*a*				19.6	116
Mn(II)	*a*				19.4	86.2
Mn(III)	*a*	18.1	7.29	13.8	18.1	11.7
Co(II)	*a*	18.8	22.3	14.1	18.8	23.7
Co(III)	*a*	19.6	15.1	14.5	19.2	59.5
None	*b*	(40.8)^e		25.1	20.0	76.9
Co(II)	*b*	17.4	5.16	13.4	18.4	2.51
Co(III)	*b*				17.6	2.27
Cu(II)	*b*	17.7	0.27	13.6	18.1	6.74
Co(II)^c	*a*	16.6	5.47			
Co(II)^c	*b*	18.4	21.0			
Co(III)^c	*a*	15.4	2.74			

[a] 1-Chlorooctane. [b] Benzene. [c] No monomer present. [d] In *n*-octane from ref 30. [e] From ref 31.

tion of the radicals through π complex formation with the aromatic solvent.[21,22] The observed trend may be simply a consequence of faster t-BHP decomposition in 1-chlorooctane. Saturated hydrocarbon solvents are known to induce hydroperoxide decomposition.[23]

The initiator efficiencies (f = number of polymer chains initiated per initiator molecule decomposed) shown in Tables I and II represent effective rather than true initiator efficiencies, since chain transfer has not been taken into account in computing these f values. In the presence of metals which catalyze t-BHP decomposition, initiator efficiency is considerably smaller than in their absence. Initiator efficiency increases in the order: Cu(II) < Co(II) < Co(III) < Mn(III) < no metal, Al(III), Ni(II), Mn(II) < Cr(III).

Osawa et al.[8b] measured t-BHP decomposition rates only in the absence of the monomer. To observe the effect of the presence of monomer, rates of decomposition were measured for Co(II) and Co(III) catalyzed systems in the absence of the monomer in benzene as well as in 1-chlorooctane. The data obtained are presented in Table III. A comparison with hydroperoxide decomposition data obtained in the presence of monomer (Tables I and II) shows a significant acceleration in the absence of monomer. Free radical addition to the monomer competing with the radical induced decomposition of the hydroperoxide could lead to this result. Metal–monomer π complex formation may also decrease the activity of the metal, decreasing the rate of hydroperoxide decomposition.

In the present experiments, uv spectra showed that Co(II) is immediately oxidized to Co(III) upon contacting t-BHP, and throughout the course of the reaction Co(II), if present, was below a detectable amount. None of the other metal systems which catalyzed t-BHP decomposition, viz., Cu(II), Mn(III), and Co(III), showed change in oxidation state. This suggests that possibly a mechanism which does not involve change in the oxidation state of the metal may be involved. Berger and Bickel[12b], Goudot,[24] and other workers[25,26] have proposed such mechanisms to account for the formation of oxygen stoichiometrically. The mechanisms involve either ligand displacement,[12b] improbable in view of the high stabilities of the acetylacetonate complexes of metals,[27] or tetracoordinate complexes of metals capable of assuming hexacoordinate configuration[24-26] by accepting two peroxide molecules as ligands. The metal serves to increase the probability of reaction and assists in electron transfer. The metal itself does not undergo any redox reaction. Among acetylacetonate complexes studied here, those of Co(II) and Cu(II) are the only ones which are tetracoordinate but are capable of bonding to two more ligands. Since Co(II) is oxidized to Co(III) in the presence of t-BHP it must assume an octahedral configuration by bonding to two t-BHP ligands. In the case of the Cu(II) complex, the driving force for the attainment of an octahedral configuration would be the stabilization obtained in this configuration from Jahn-Teller distortion. It must be pointed out that some of the metal catalyzed t-BHP decomposition does seem to take place through a radical mechanism, since an increased rate of t-BHP decomposition does result in an increased rate of initiation, as indicated by the observed decrease in molecular weight of the polymer formed. The observed result can also be explained by a reaction path which would involve coordination of two t-BHP ligands to Cu(II) or Co(II) acetylacetonate, as suggested above, with the difference that these ligands may also react to give free radical products. The decreased initiator efficiency in the presence of active metals could result from peroxy radical–metal complexes.[28]

Variation of the logarithms of rates of hydroperoxide decomposition (R_d) and polymerization (R_p) with reciprocal temperature has been utilized to obtain activation energies and frequency factors for hydroperoxide decomposition (E_d, A_d) and polymerization (E_a, A). Table IV shows these data along with E_a values calculated from E_d, using the relation:

$$E_a = E_p + (E_d - E_t)/2$$

where the activation energy for propagation (E_p) and that for termination (E_t) are considered to have values of 4.7 and 0 kcal/mol, respectively.[29] The correspondence between the observed and calculated values of E_a for metal catalyzed systems is not good. A similar trend has been observed by Osawa et al.[8b] who suggest that E_p and E_t values may be different in these systems. The observed discrepancy could also be due to a significant wastage of the initiator.

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