Electronic Spectra of Copper(II) Acetylacetonates and Their Activity as Initiators of the Polymerization of Styrene

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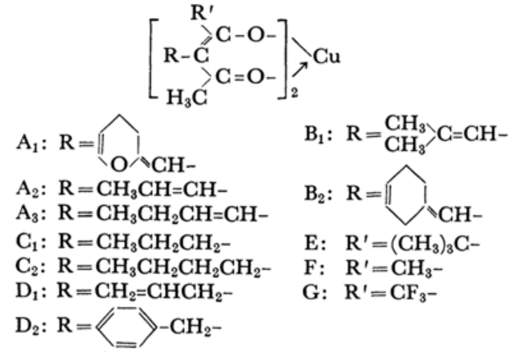
In a preceding communication,[1] we reported that copper(II) chelates A showed a high activity as initiators of the radical polymerization of styrene and methyl methacrylate. The polymerization proceeds *via* the reduction of Cu(II), and the ligand is incorporated into the polymer chain.

As is shown in Table 1, the order of the activity in initiation of the polymerization of styrene is as follows:

$$A>B>C>D>E>F>G$$



(A—D, $R'=CH_3$; E—G, R=H)

TABLE 1. RATE OF BULK POLYMERIZATION OF STYRENE INITIATED BY COPPER(II) CHELATES AT 80°C AND THE ULTRAVIOLET ABSORPTION BAND(III) OF THE CHELATES IN CHLOROFORM

Cu(II)	Chelate (mol/l)[a]	Rate of Polymerization (wt%/hr)	λ_{max} (mμ)	ε_{max}
A_1	0.0137	11.90	312	20300
A_2	0.0135	6.20	312	23400
A_3	0.0137	8.70	312	24500
B_1	0.0135	3.30	312	25600
B_2	0.0139	2.70	312	25700
C_1	0.0068	1.30	312	27100
C_2	0.0068	1.40	312	27100
D_1	0.0068	1.00	309	30300
D_2	0.0068	1.05	309	28600
E	0.0068	0.80	299	22900
F	0.0068	0.60	297	25100
G	0.0068	0.30	300	22100
None	—	0.60	—	—

a) Concentration of chelate added in the polymerization.

Figure 1 presents the visible spectra of these chelates in chloroform. The marked color changes from G to A upon the substitution of the hydrogen of F, $Cu(acac)_2$, are associated with the ultraviolet tail of the first allowed electronic absorption band (Band III in terms of the notation of a recent paper[2]; it occurs at ~300 mμ). Table 1 lists the wave lengths and intensities observed for Band III in chloroform.

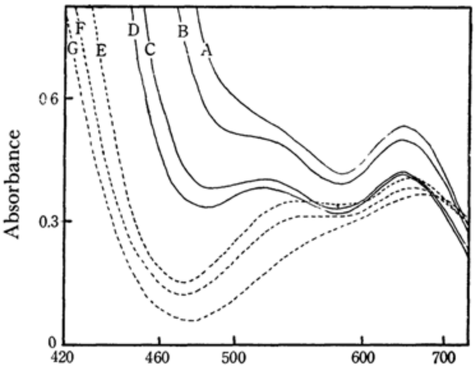


Fig. 1. Visible spectra of copper(II) chelates in chloroform.
[Cu(II) chelate]=0.01 mol/l

It is observed that the Band III of the chelate A is most remarkably broadened and that the tail extends considerably into the visible region of the spectrum. The order of the magnitude of the broadening of Band III upon substitution and the extending of the ultraviolet tail into the visible region seem to be as follows:

$$A>B>C>D>E(>F)>G$$

This order is essentially the same as the order of the activity in the polymerization. A similar broadening is also observed in the visible spectra of the chelate F with a rise in the temperature, this compound being known as a thermochromic substance.[3,4]

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[4] K. Sone, K. Mizutani and T. Sakai, Proceeding of the X. ICCC, Tokyo-Nikko (1967), p. 138.