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Vinyl Polymerization by Metal Complexes. XV.* Polymerization of Acrylonitrile Initiated by Imidazole-Copper(II) Complex

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ABSTRACT

The polymerization of acrylonitrile initiated with the imidazole-copper(II) complexes was studied in dimethylsulfoxide solution. The ability of the complexes to initiate polymerization seems to depend on their anion. 2-Substituted imidazole-copper(II) complexes of the type, CuL_4X_2 (L = imidazole as ligand and X = anion), were also found to initiate vinyl polymerization. From the data of electronic spectra in dimethylsulfoxide solution, the initiation mechanism is discussed in terms of the formation of the active species by the interaction of the complex with monomer molecules.

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INTRODUCTION

Imidazole is a compound of considerable interest as a ligand in that its presence in many biological systems provides a potential binding site for metal ions. A limited amount of work has been published on the complexes of transition metals with imidazole and its derivatives [1-3], and the complexing properties of such imidazole ligands, both in solution and in the solid state, have been studied [4, 5].

Previously, one of the authors reported that imidazole could initiate vinyl polymerization by a free radical mechanism in the presence of carbon tetrachloride, and the reaction mechanism was discussed [6, 7]. Very recently, kinetics of the reaction of imidazole with acrylonitrile was studied by using NMR [8]. However, very little has hitherto been known about the initiation behavior of the metal complexes of imidazole and its derivatives. The present paper concerns the free radical initiation of some vinyl monomers, especially acrylonitrile, by the imidazole-cupric ion system in dimethylsulfoxide solution.

EXPERIMENTAL

Reagents

Imidazole and 2-substituted imidazoles, which were used as ligands, were purified thrice by recrystallization from benzene, ethanol, or ethyl ether. Acrylonitrile monomer and dimethylsulfoxide (DMSO), N, N'-dimethylacetamide (DMA), dimethylformamide (DMF), and hexamethylphosphoramide (HMPA) were purified by repeated distillations under reduced pressure. Copper salts were analytical grade of commercial origin and used without further purification.

Synthesis of Imidazole-Copper(II) Complexes

The imidazole-copper(II) complexes were prepared by modifying the method of Eilbeck et al. [4]: 2 g of imidazole was dissolved in 10 ml of ethanol. To this solution, 1.8 g of $Cu(NO_3)_2 . 3H_2O$ in 10 ml ethanol were added dropwise with stirring. The product immediately precipitated as a blue-violet crystal. Stirring was continued for several minutes, and the mixture allowed to stand for 24 hr. The product was then filtered off, and after thorough washing with a small amount of ethanol and ethyl ether, the crystals were dried over phosphorus pentoxide in a desiccator.

Synthesis of the 2-substituted imidazoles was reported earlier [1].

Polymerization of Acrylonitrile

Polymerization was carried out in sealed tubes by the method reported previously [6, 7]. The imidazole-copper(II) complex and the monomer in solution were put into a tube. After thorough evacuation, the sealed tube was shaken in a thermostat maintained at 50°C for a given time. The content was then poured into an excess of methanol to precipitate the polymer. The degree of polymerization was measured by viscometry in DMF solution at 25°C.

Electronic Spectra Measurement

Electronic spectra of the samples were measured between 800 and 200 nm, by using a Hitachi 124-type spectrophotometer.

RESULTS AND DISCUSSION

Polymerization of Acrylonitrile Initiated by Imidazole-Copper(II) Complex

The polymerization of acrylonitrile was first carried out at 60°C in the presence of different imidazole-copper(II) ion complexes. Table 1 shows the λ_{max} and ϵ_{max} values in the electronic spectra of the copper complexes. As shown in Table 1, polymerization of acrylonitrile could be initiated in the presence of different imidazole-copper(II) ion complexes. It was also confirmed that polymerization could be initiated only to low conversion when the reaction system was devoid of either imidazole or cupric ion. The initiation ability of these complexes seems to depend on the anion of the copper(II) salts; that is, copper perchlorate and nitrate could initiate the polymerization, while copper halides such as chloride and bromide could not initiate the polymerization.

These results may be explained by differences in the structure of the copper complexes. For the comparison of the electronic spectra of these imidazole complexes, the λ_{max} values of the absorption of

TABLE 1. Polymerization of Acrylonitrile by Imidazole-Copper(II) Complexes (in DMSO Solution for 2 hr)[a]

Complex	λ_{max} (ϵ) in DMSO (nm)	Conversion (%)
$[Cu(ImH)_4(NO_3)_2]$	660 (47), 275 (1130)	32.6
$[Cu(ImH)_4(ClO_4)_2]$	660 (47), 280 (1120)	35.0
$[Cu(ImH)_2(NO_3)_2]$	730 (80), 275 (2340)	27.4
$[Cu(ImH)_4Cl_2]$	770 (82), 293 (1842)	0
$[Cu(ImH)_2Cl_2]$	770 (101), 295 (1622)	0
$[Cu(ImH)_4Br_2]$	740 (78), 288 (1438)	0
$[Cu(ImH)_2Br_2]$	760 (913), 285 (2419)	0
$[Cu(ImH)_2]$	-[b]	0.2
ImH	-	Trace
$Cu(NO_3)_2.3H_2O$	-	0.8
$Cu(ClO_4)_2.6H_2O$	-	0.2
$CuCl_2$	-	0
$CuBr_2$	-	0

[a] [I] = 2 × 10^{-2} mole/liter, [AN] = 3.04 mole/liter.
[b] Insoluble in DMSO at 60°C.

d-d ligand fields of perchlorate and nitrate were found to be much different from those of the halides. The electronic spectra of the nitrate and chloride of complexes of the type $Cu(ImH)_4X_2$ measured in DMSO solution, in which ImH and X denote imidazole and ligand, respectively, are shown in Fig. 1 as an example.

As can be seen from Fig. 1, the λ_{max} of the d-d absorption band exists at 650 nm for nitrate and at 770 nm for chloride. It is known that these two complexes of the type $Cu(ImH)_4X_2$ are in a tetragonally distorted octahedral environment, in which the imidazole ligand lies in the xy plane with the anions above and below the distorted octahedral structure. The distance from copper atom in the xy plane to the anion on the z axis is longer for the copper-nitrogen bond than for the copper-chlorine bond, because nitrate group is more weakly coordinated to the copper atom than is the chlorine

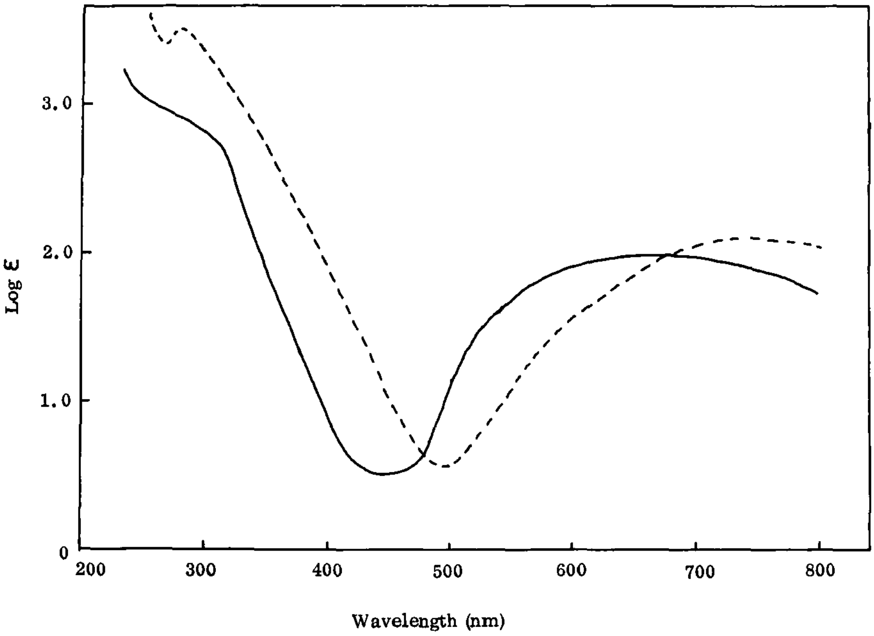


FIG. 1. Electronic spectra of $[Cu(ImH)_4]X_2$ complexes in DMSO: (——) X = NO_3^-; (- -) X = Cl^-.

atom. $Cu(ImH)_4(NO_3)_2$ shows a λ_{max} of the d-d absorption band at 620 nm in methanol and at 630 nm in ethanol solutions. Coordination of the nitrate anion on the z axis in these solutions is assumed to be very weak, and the structure of the complex presumably exists in the form of a typical tetragonal plane around the copper atom. In DMSO solution the shift of the λ_{max} value of about 20 nm toward a longer wavelength was observed, which may show that equilibrium between the nitrate anion and the solvent exists. The case of the perchlorate anion is similar. On the other hand, λ_{max} exists at 770 nm, that is, in the longer wavelength range in the case of chloride and bromide anions, which suggests that chloride bonds more strongly with copper atom than the nitrate anion does, and it is assumed that copper exists as a form of the copper complex with an octahedral structure. The shift of λ_{max} was not observed in this case, even in DMSO solution, which suggests that the bond between copper and chlorine atoms is too strong to cause exchange of the latter with the solvent.

From these findings it became obvious that the presence of the copper(II) complex is necessary for the polymerization of acrylonitrile, in which the xy plane consists of a central copper atom bonded with –NH– groups of imidazole molecules, and the DMSO molecules exist on the z axis and is coordinated with the copper atom.

Co(II), Ni(II), and Zn(II) complexes with imidazoles were found to be unable to initiate the polymerization of acrylonitrile. This fact might be explained by the differences in the structures of the complexes. Co(II) and Ni(II) are known to form the typical octahedral ML_6X_2 type of complex, and Zn(II) for the tetrahedral ML_4X_2 type of complex [4], which are different from the copper complex, and this fact might be reflected in the difference in reactivity for initiating polymerization.

From the results shown in Table 1 it is clear that polymerization could be initiated more smoothly with $Cu(ImH)_2(NO_3)_2$ than with $[Cu(ImH)_2]^0$, which suggests the important role of the NH protons in the imidazole ring coordinated with copper(II) ion for initiating polymerization. Therefore, the polymerization of acrylonitrile initiated by $[Cu(ImH)_2]^0$ was next carried out in the presence of different amounts of imidazole at 60°C. Plots of the rate of polymerization vs [imidazole]/[complex] are shown in Fig. 2, in comparison with the case in which $Cu(ImH)_4(NO_3)_2$ was used as the imidazole-copper(II) complex. From Fig. 2 it is apparent that the rate of polymerization was not affected by the presence of imidazole additionally present in the reaction system. In the case of $[Cu(ImH)_2]^0$, the complex is too stable to bind imidazole by coordination, which is also supported by the fact that no color change was observed during polymerization. In the case of $Cu(ImH)_4(NO_3)_2$, imidazole cannot be coordinated on the z axis of the copper(II) plane, but does exist as a form of free compound, which was shown spectrophotometrically. In conclusion, it was proved that the NH protons coordinated with the copper(II) ion, not the protons of free imidazoles, are necessary for initiating the polymerization of acrylonitrile.

Polymerization of Acrylonitrile Initiated by 2-Substituted Imidazole-Copper(II) Ion Complex

The polymerization of acrylonitrile was carried out at 50°C in DMSO solution in the presence of different 2-substituted imidazole-copper(II) complexes of the type CuL_4X_2, in which 2-methyl-, 2-ethyl-, 2-phenyl-, and 2-ethyl-4-methylimidazoles were chosen as the ligands.

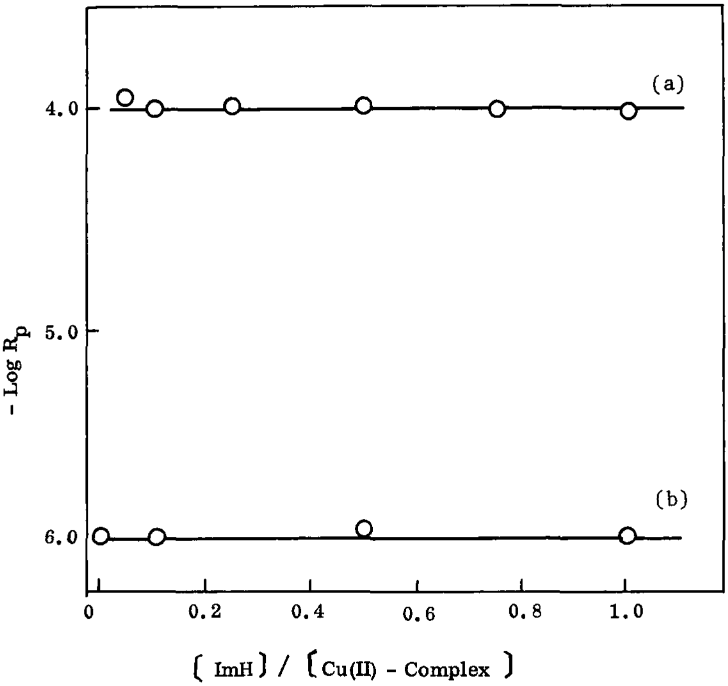


FIG. 2. Effects of free imidazole on the rate of polymerization of acrylonitrile by $Cu(ImH)_4(NO_3)_2$ and $Cu(ImH)_2$ in DMSO solution at 60°C. $[I] = 2 \times 10^{-2}$ mole/liter, $[AN] = 3.04$ moles/liter.

The results are shown in Table 2. In the case of both nitrate and perchlorate, conversion was found to be in the order: 2-ethyl > 2-methyl > (H) > 2-ethyl-4-methyl ≫ 2-phenyl. The molecular weight of the polymer obtained was in the order: 2-methyl, (H) > 2-ethyl, 2-ethyl-4-methyl.

The results suggest here also that the conversion could be correlated with the λ_{max} value of the d-d absorption band in dimethylsulfoxide solution. The λ_{max} of the d-d absorption band is plotted against the rate, R_p, in Fig. 3. In order to clarify the relationship between the planarity of the xy plane and the ability of the complexes to initiate polymerization, a more detailed study is necessary

TABLE 2. Polymerization of Acrylonitrile by Cu [Substituted $(ImH)_4X_2$][a]

R	X	λ_{max} (ϵ) in DMSO (nm)	Conversion (%)	$\overline{M}_w \times 10^{-5}$
H	NO_3^-	650 (45), 275 (1130)	22.2	5.4
	ClO_4^-	650 (46), 275 (2340)	30.9	5.3
2-Methyl	NO_3^-	660 (84), 290 (7080)	28.6	5.5
	ClO_4^-	660 (88), 284 (8160)	34.8	5.4
2-Ethyl	NO_3^-	674 (73), 288 (6300)	57.0	4.3
	ClO_4^-	670 (77), 287 (6580)	46.0	4.4
2-Ethyl-4-methyl	NO_3^-	670 (78), 299 (1460)	27.3	4.0
	ClO_4^-	678 (60), 300 (1650)	25.1	4.6
2-Phenyl	NO_3^-	773 (50), -	2.4	-
	ClO_4^-	770 (52), -	0.1	-

[a] [I] = 1×10^{-2} mole/liter, [AN] = 3.04 mole/liter, 50°C in DMSO solution.

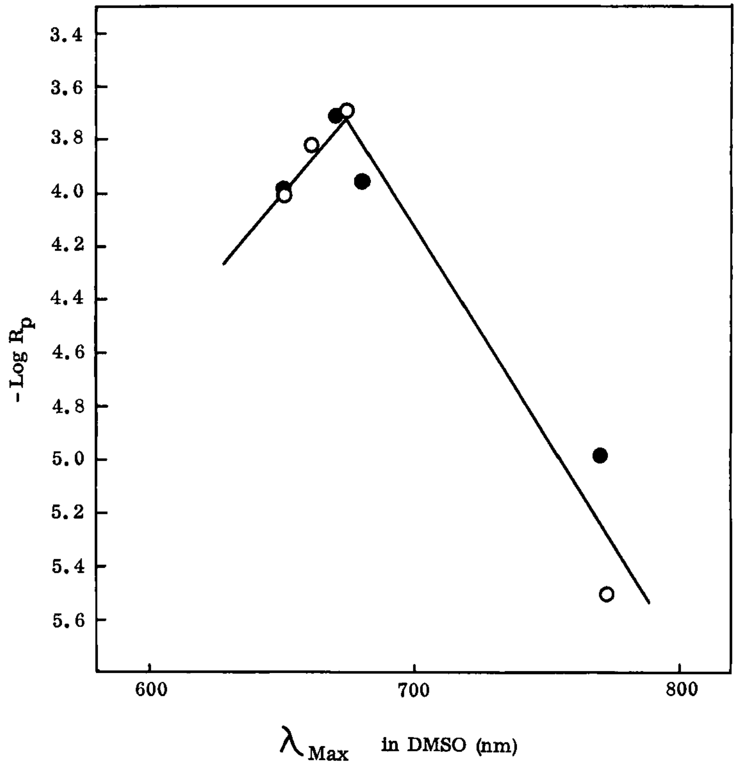


FIG. 3. The rate of polymerization R_p vs λ_{max} of Cu(II) complexes in DMSO solution: (●) ClO_4^-, (○) NO_3^-.

Interaction between Imidazole-Copper(II) Complex and Solvents or the Monomer

The polymerization of acrylonitrile initiated by $Cu(ImH)_4(NO_3)_2$ complex was carried out in different solvents. As can be seen from Table 3, polymerization proceeded only in aprotic polar solvents such as DMSO, DMA, DMF, and HMPA solution. The conversion was found to be as in the order: in DMSO $\gg$ in HMPA $\simeq$ in DMF, DMA.

Thus the effect of DMSO on polymerization appeared to be primary. Figure 4 shows the rate of polymerization carried out in DMA

TABLE 3. Polymerization of Acrylonitrile by $Cu(ImH)_4(NO_3)_2$ in Various Solvents[a]

Solvent	λ_{max} of d-d band (nm)	Conversion (%)	$[\eta]$
DMSO	650	22.2	1.39
DMA	645	9.3	0.72
DMF	620	9.3	0.68
HMPA	675	10.0	0.25
Methanol	612	0	-
Ethanol	630	0	-
Water	620	0	-
None	600	0	-

[a] [I] = 1 × 10^{-2} mole/liter, [AN] = 3.04 mole/liter, 50°C, for 2 hr.

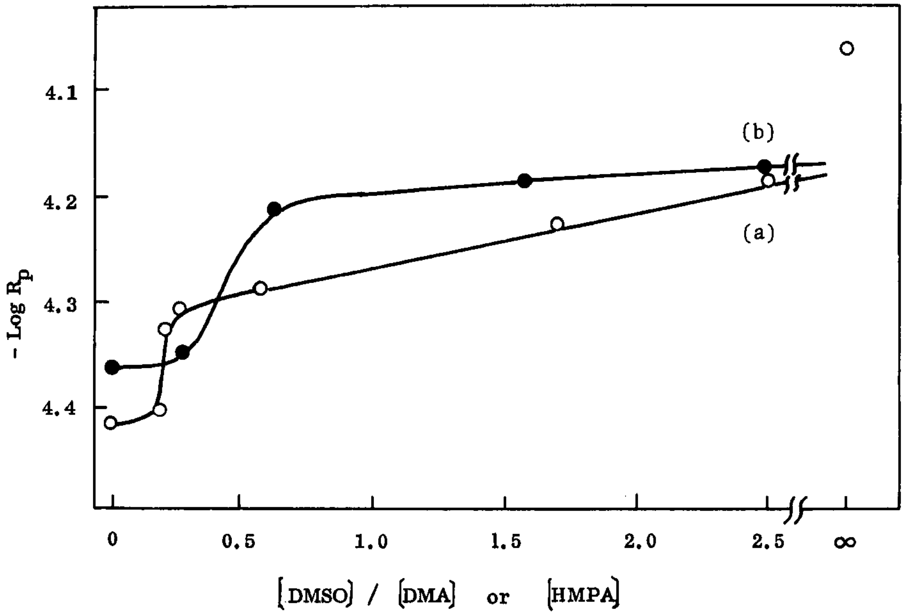


FIG. 4. Effects of DMSO on the rate of polymerization of acrylonitrile by $[Cu(ImH)_4(NO_3)_2]$ in DMA and HMPA solutions, 50°C. (a) DMA, (b) HMPA, [I] = 1 × 10^{-2} mole/liter, [AN] = 3.04 moles/liter.

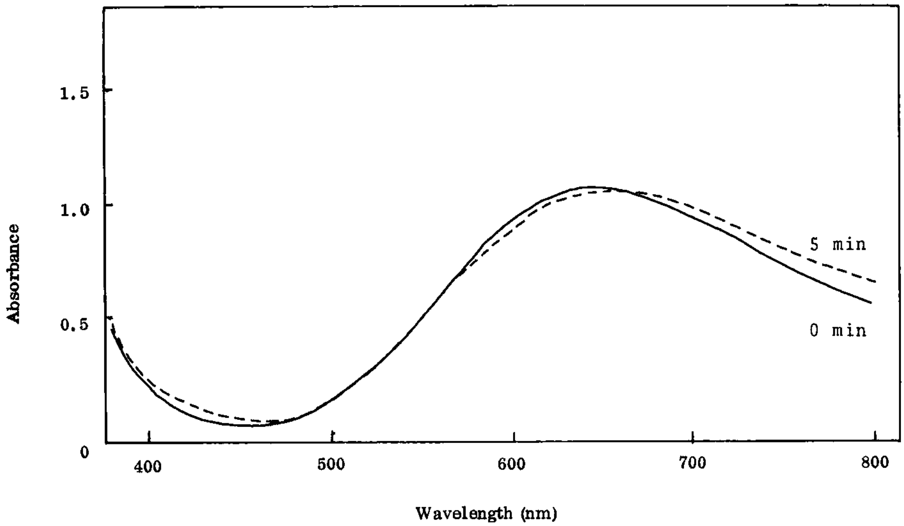
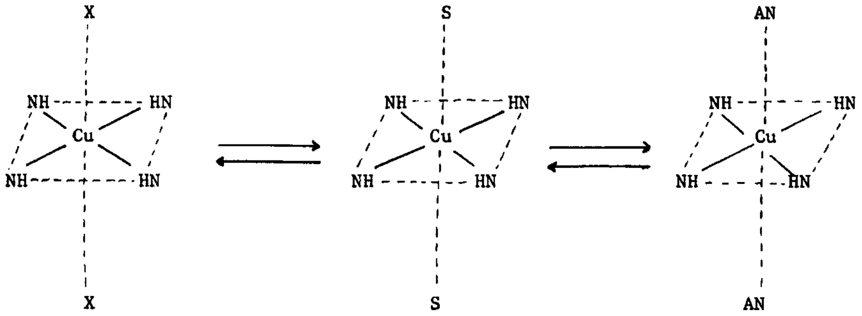


FIG. 5. Electronic spectra of the $Cu(ImH)_4(NO_3)_2$/acrylonitrile system in DMSO solution at 50°C. [I] = 2×10^{-2} mole/liter, [AN] = 3.04 moles/liter.

and HMPA solutions in the presence of different amounts of DMSO. The rate was found to increase linearly when the concentration ratio of [DMSO]/[solvent] exceeded about 0.3 to 0.6. From these results it becomes apparent that the strong solvation of the solvents to the copper(II) complex is essential for initiating polymerization, and solvation was greatest in the case of DMSO.

Figure 5 shows the electronic spectra of the $Cu(ImH)_4(NO_3)_2$-acrylonitrile system at 50°C in DMSO solution. From Fig. 5 it can be seen that λ_{max} of the d-d absorption band shifts to the longer wavelength side while decreasing its ϵ_{max} value. In the absence of acrylonitrile, the shift of λ_{max} value was not observed. This change could only be seen in the case when polymerization could proceed; for example, in the presence of perchlorate anion, whereas it could not be observed in the presence of halogen anions. From these findings it is suggested that when acrylonitrile polymerization was initiated by imidazole-copper(II) complexes the following equilibrium relationship exists between anions of the complex and the monomer at the early stage of polymerization, which leads to the formation of active species which are capable of initiating polymerization.



X = NO_3^-, ClO_4^-, Cl^-, Br^-; S = aprotic polar solvents

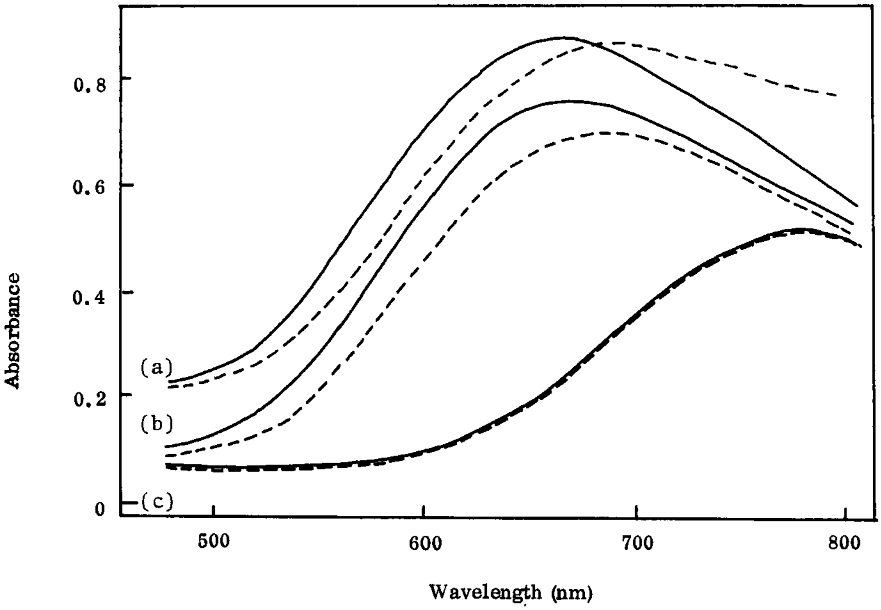


FIG. 6. Electronic spectra of the $Cu(ImH)_4(NO_3)_2$/acrylonitrile system in DMSO solution at 50°C. [I] = 1×10^{-2} mole/liter, [AN] = 3.04 moles/liter, (—) 0 min, (- -) 10 min, R = methyl (a), ethyl (b), and phenyl (c).

To summarize, the ability of the imidazole-copper(II) complex to coordinate with a ligand along the z axis on the xy plane is apparently in the order: Cl^-, $Br^- \gg NO_3^- > ClO_4^-$. In the case in which halogen anions such as Cl^- and Br^- are present in the system, no polymerization is initiated because they cannot be replaced by acrylonitrile monomer, even in solvents with a rather strong solvating force. Furthermore, in solvents with weaker solvating forces such as methanol, ethanol, and water, the monomer also cannot be replaced by the solvent, which cannot lead to polymerization.

Figure 6 shows the electronic spectra of the 2-substituted imidazole-copper(II) complexes of the type CuL_4X_2 ($X = NO_3^-$), in the range of the d-d absorption band. This result seem to support the conclusion reached above.

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