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POLYMERIZABLE & POLYMERIC

TYPE I & TYPE II PHOTOINITIATORS

by

SANDRALEE PATRICIA LEWIS

A thesis submitted for the degree of Doctor of Philosophy (PhD) in the Chemistry Department of the City University, London.

April 1992

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VOLUME

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CHAPTER V:

POLYMERIZABLE TYPE I & TYPE II PHOTOINITIATORS

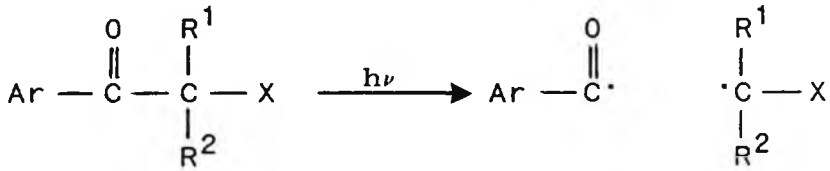
5.1 **INTRODUCTION**

Photoinitiators for free radical polymerization can generate initiating radicals by:

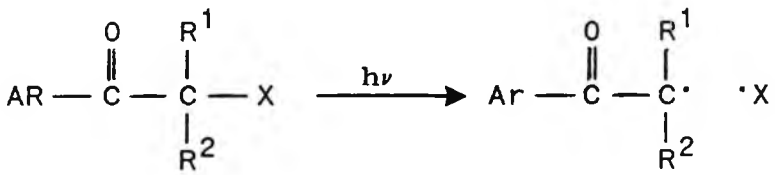
(i) direct photofragmentation (unimolecular cleavage)

or (ii) a bimolecular reaction

Direct photofragmentation mechanisms can generally be classed as α-cleavage (Norrish Type I) or β-cleavage mechanisms.



α- Cleavage



β- Cleavage

Benzoin and its esters and ethers have been shown to undergo α-cleavage upon photolysis[1-4]. Photoinitiators of

this type were among the first to be patented for use in free radical polymerizations, and find wide use in applications in the printing and surface coatings industries. Benzils, on the other hand, generate initiating radicals by initial hydrogen abstraction from a donor[4,5].

Polymeric photoinitiators carrying benzoin side-chain moieties have been prepared and have been found to initiate the photopolymerization of vinyl monomers with high efficiency[6]. Polymeric photoinitiators with either benzoin or benzil moieties built into the backbone have not, however, been investigated to any appreciable extent.

In order to produce polymeric photoinitiators with the photoreactive aromatic ketone moieties incorporated into the backbone it was decided to prepare benzil and benzoin derivatives substituted at the 4 and 4' positions. Reaction of these monomers with a suitable disubstituted reagent should then afford polymeric materials of the desired structure. In this chapter the preparation of a number of 4,4'-disubstituted benzils and benzoins is described. Having prepared these potentially photoreactive monomers, it was then decided to investigate the efficiency with which they may function as initiators for the photopolymerization of vinyl monomers.

5.2 EXPERIMENTAL

All NMR spectra were recorded on a Jeol JNM-PMX 60 SI spectrometer (unless otherwise stated), with tetramethylsilane (supplied by Aldrich Chemical Company) as the internal standard.

IR spectra were recorded on a Perkin-Elmer 983 G infra-red spectrophotometer.

UV spectra were recorded on a Philips PU 8720 UV/visible scanning spectrophotometer.

Melting points were determined by means of a Griffin P.1158 melting point apparatus.

UV curing measurements were performed with a Colordry unit composed of two medium pressure 80W cm^{-1} mercury lamps over a moving belt apparatus. For the tests carried out, only one of the two lamps was used. Solutions were coated onto a substrate of G.N.T. paper (supplied by Wiggins-Teape, U.K.), which was then attached to a metal plate before being placed on the moving belt. Wet film thicknesses were determined by K-bars supplied by R.K. Print-Coat Instruments Ltd., U.K.

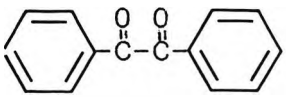
Real-time infra-red spectra were recorded on a Perkin-Elmer 599 infra-red spectrophotometer. An Osram HBO 100 W/2 mercury lamp was used as the UV source (for schematic arrangement see p.160).

Mass spectra were recorded by means of a Kratos MS 30 apparatus with a DS 50 data system.

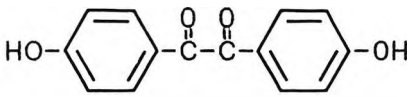
The following abbreviations are used to represent solvents for spectral and T.L.C. analysis:

DMF	-	Dimethylformamide
$CHCl_3$	-	Chloroform
MeOH	-	Methanol
DMSO	-	Dimethylsulphoxide
$CDCl_3$	-	Deuterated chloroform
Acetone-d_6	-	Deuterated acetone
DMSO-d_6	-	Deuterated dimethylsulphoxide
THF	-	Tetrahydrofuran

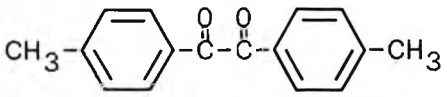
Monomeric Benzil Derivatives



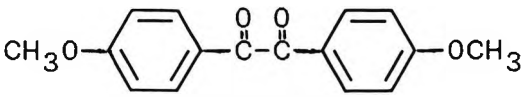
Benzil
I



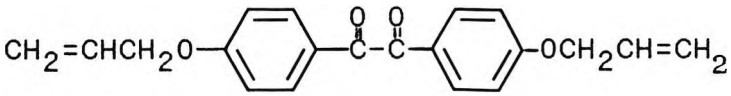
4,4'-Dihydroxybenzil
II



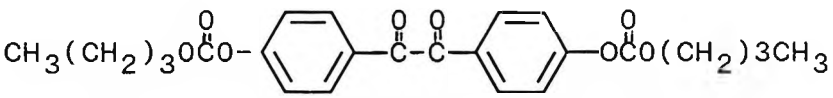
4,4'-Dimethylbenzil
III



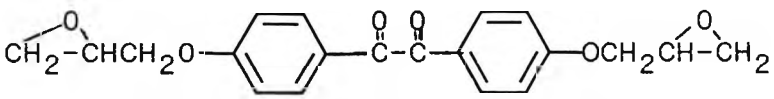
4,4'-Dimethoxybenzil
IV



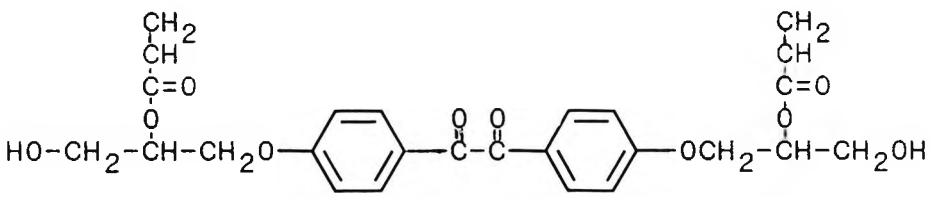
Benzil-4,4'-Diallyloxy Ether
V



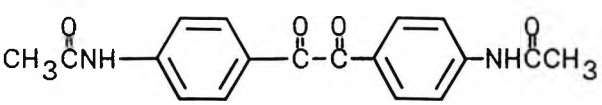
Benzil-4,4'-Bis(n-Butyl Carbonate)
VI



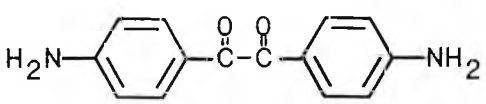
Benzil-4,4'-Diglycidyl Ether
VII



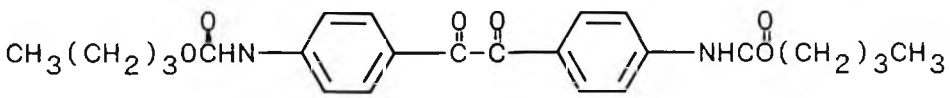
4,4'-Bis[(2-Acrylate-3-Hydroxy)Propoxy]Benzil
VIII



4,4'-Diacetamidobenzil
IX



4,4'-Diaminobenzil
X



Benzil-4,4'-Bis(n-Butyl Urethane)
XI

5.2.1 PREPARATION OF MONOMERIC BENZIL DERIVATIVES

Substituted benzils are most commonly prepared by oxidation of their benzoin analogues[2]. However, since the corresponding benzoin derivatives were not available, the majority of the benzils tested in the following pages were prepared by other means. In practise, it was found that 4,4'-dihydroxybenzil was extremely useful as a starting material, with many of the desired benzil derivatives being obtained by reaction of the two hydroxyl groups with suitable reagents.

I : Benzil

This was purchased from Aldrich Chemical Company and was used without further purification.

II : 4,4'-Dihydroxybenzil

Attempts to demethylate 4,4'-dimethoxybenzil (supplied by Aldrich Chemical Company) with a mixture of chlorotrimethylsilane and sodium iodide[8] led to the formation of a complex mixture. A variety of solvent combinations failed to produce a reasonable chromatographic separation of

the components of the mixture. Similar problems arose when using boron tribromide as the demethylating agent. A successful demethylation of 4,4'-dimethoxybenzil was effected, however, using hydrobromic acid as the demethylating agent.

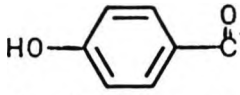
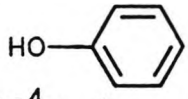
Procedure

150ml 48% hydrobromic acid were added to a solution of 5.41g (0.01 mol) 4,4'-dimethoxybenzil in 60ml acetic acid. The resulting mixture was heated under reflux overnight, after which time T.L.C. analysis (CH_2Cl_2/MeOH 99:1) showed the reaction to be complete. The mixture was diluted with 300ml water and left to stand at room temperature. The solid precipitate which formed upon standing was isolated by filtration and dissolved in ether. The ethereal solution was washed with water and dried over anhydrous sodium sulphate. Solvent evaporation in vacuo afforded a yellow solid in 76% yield with a melting range of 250-252°C (literature value[9] 253°C).

NMR spectrum (Acetone-d_6) : δ 7.85-7.77 (d,4H,J=8Hz: benzoyl); 7.07-6.90 (d,4H,J=8Hz; aryl);

IR Spectrum (KBr Disc) : 3415 (H-bonded O-H str.); 1642

(ketone C=O str.); 1598, 1570, 1513 & 1444 (aryl C-C str.); 1294 & 1158 (phenol C-O str./O-H def.); 842 (p-disubstituted aromatic out-of-plane C-H def.) cm^{-1}.

Mass Spectrum : m/z (int:) : 242 (1.8; M^+) 121 (100.0 ; ); 93 (12.7;  +);

UV Spectrum (DMF): $n-\pi^*$ $\varepsilon = 2.0 \times 10^4$; $\lambda_{max} = 301nm$

Hydrobromic acid and 4,4'-dimethoxybenzil were supplied by Aldrich Chemical Company and were used without further purification.

Dichloromethane, methanol and diethyl ether were all supplied by BDH and were also used without further purification.

Acetone-d_6 was supplied by Aldrich Chemical Company.

III & IV : 4,4'-Dimethylbenzil & 4,4'-Dimethoxybenzil

Both of these compounds were supplied by Aldrich Chemical Company and were used without further purification.

V : Benzil-4,4'-Diallyloxy Ether

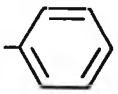
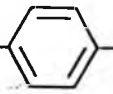
Procedure

2.02g (0.008 mol) 4,4'-dihydroxybenzil, 2.30g (0.017 mol) anhydrous potassium carbonate and 2.2g (0.018 mol) allyl bromide were heated under reflux in dry acetone. After two hours the mixture was removed from the heat and allowed to cool to room temperature. The reaction mixture was diluted with 10ml water and extracted with two 20ml portions of ether. The combined ether extracts were washed with 10ml 10% aqueous sodium hydroxide and dried over 1.5g anhydrous potassium carbonate. The yellow solid afforded by solvent evaporation of the ethereal solution was recrystallized from ethanol in 68% yield. Melting range = 113-114°C (literature value[10] 115-116°C).

NMR Spectrum (Acetone-d_6) : δ 8.00-7.78 (d,4H,J=8Hz: benzoyl); 7.30-7.03 (d,4H,J=8Hz; aryl); 6.77-5.82 (m,2H,2x =CH-); 5.63-5.15 (m,4H,2x CH_2=); 4.85-4.67 (d,4H,J=5Hz; 2x -CH_2O-);

IR Spectrum (KBr Disc) : 1657 (ketone C=O str.); 1599, 1570 & 1507 (aryl C-C str.); 1421 (CH_2=CH- C-H def.); 1263 (alkyl aryl ether C-O str); 998 (CH_2=CHR out-of-plane C-H def.); 840 (p-disubstituted aromatic out-of-plane C-H def.); cm^{-1}

Mass Spectrum : m/z (int:) : 322(0.4; M^+); 161(100.0; $M^+/2$);

133 (1.4 ; CH_2=$CHCH_2O$-  +); 121 (14.2; HO-  -C+);

58 (1.0 ; CH_2=$CHCH_2OH$);

UV Spectrum (Acetone): n-π^* λ_{max} = 330nm; ε= 3.9 x 10^3

4,4'-Dihydroxybenzil was prepared as previously described. Allyl bromide was supplied by Aldrich Chemical Company. Sodium hydroxide and anhydrous potassium carbonate were supplied by BDH.

VI : Benzil-4,4'-Bis(n-Butyl Carbonate)

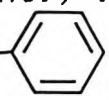
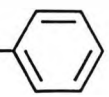
Procedure

7.26g (0.03 mol) 4,4'-dihydroxybenzil were dissolved in tetrahydrofuran and added to a solution of 1.2g sodium hydroxide in 6ml water. 4.23ml (0.03 mol) n-butylchloroformate were added dropwise to the stirred tetrahydrofuran solution. A further 1.2g sodium hydroxide in 6ml water and 4.23ml n-butylchloroformate were added after stirring at room temperature for three hours, monitoring by T.L.C. (CH_3Cl_2/MeOH 99:1). Stirring at room temperature was continued overnight before adding a final 1.2g sodium hydroxide in 6ml water and 4.23ml n-butylchloroformate. After stirring at room temperature for

a further 60 hours the solution was refrigerated, leading to solidification of the organic layer. The aqueous layer was then decanted off and the organic layer was allowed to warm to room temperature. The tetrahydrofuran solution was dried over anhydrous sodium sulphate before removing the solvent in vacuo. The yellow oil thus formed quickly solidified on standing and was recrystallized from ethanol in 52% yield. The needle-like crystals were found to have a melting range of 59-60°C.

NMR Spectrum (Acetone-d_6) : δ 8.20-7.93 (d,4H,J=8Hz: benzoyl); 7.67-7.32 (d,4H,J-8Hz; aryl); 4.48-4.13 (t,4H,J=6Hz; 2x-CH_2CO_2-); 1.90-1.10 (m,8H,4x-CH_2-); 1.10-0.67 (m,6H,2xCH_3-);

IR Spectrum (kBr Disc) : 2964 & 2867 (alkyl C-H str.); 1768 (ester C=O str.); 1668, (ketone C=O str.); 1601, 1586 & 1501 (aryl C-C str.); 1397 (CH_3- antisymm.C-H def.); 853 (p-disubstituted aromatic out-of-plane C-H def.) cm^{-1}.

Mass Spectrum : m/z (int:) : 442 (0.02; M^+) 221 (33.74; $M^+/2$); 121 (100.00; HCO_2-  +); 93 (5.20; HO-  +); 57 (6.90; $CH_3(CH_2)_2CH_2^+$)

UV Spectrum (Acetone): $n \rightarrow \pi^*$ ε = 234 ; λ_{max} = 326nm

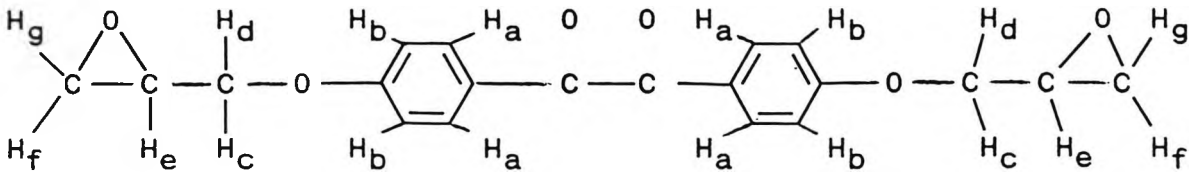
n-Butylchloroformate and acetone-d_6 were supplied by Aldrich Chemical Company and were used without further purification. Sodium hydroxide was supplied by BDH.

VII : Benzil-4,4'-Diglycidyl Ether

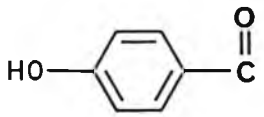
Procedure

2.42g (0.010 mol) 4,4'-dihydroxybenzil, 8.14g (0.088 mol) epichlorohydrin and 20ml isopropanol were heated to 75°C. 0.88g 50% sodium hydroxide was added dropwise to the stirred reaction mixture and the temperature was increased to 83°C for four hours. The reaction mixture was allowed to cool before being diluted with water. Conventional work-up (ether extraction, drying and evaporation of solvent) yielded a yellow oil, which solidified on overnight refrigeration and was recrystallized from chloroform/ethanol 1:2 in 45% yield with a melting range of 128 - 130°C (literature value[11] 120-130°C).

NMR Spectrum ($CDCl_3$) : δ 7.95-7.92 (d,4H,J=8Hz: H_a); 6.99-6.95 (d,4H,J=8Hz; H_b); 4.37-4.32 (m,2H,H_d); 4.02-4.00 (m,2H,H_c); 3.41-3.38 (m,2H,H_e); 2.96-2.92 (m,2H,H_f); 2.80-2.77 (m,2H,H_g)



IR Spectrum (KBr Disc) : 3073 (epoxide C-H str.); 3009 (aryl C-H str.), 1659 (ketone C=O str.); 1599, 1570, & 1507 (aryl C-C str.); 1261 (alkyl aryl ether C-O str.); 848 (p-disubstituted aromatic out-of-plane C-H def.) cm^{-1}

Mass Spectrum : m/z (int:) : 354 (3.2; M^+) ; 177 (100.0; $M^+/_2$); 121 (62.5; ); 57 (22.5; $CH_2\text{-}\overset{O}{C}H\overset{+}{C}H_2$);

UV Spectrum ($CHCl_3$): $n\text{-}\pi^*$ λ_{max} = 300nm, ε = 2.3 x10^4

Epichlorohydrin, isopropanol and deuterated chloroform were supplied by Aldrich Chemical Company and were used without further purification.

The NMR spectrum was recorded on a Bruker WH 270 spectrometer.

VIII : 4,4'-Bis[(2-Acrylate-3-Hydroxy)Propoxy] Benzil

Procedure

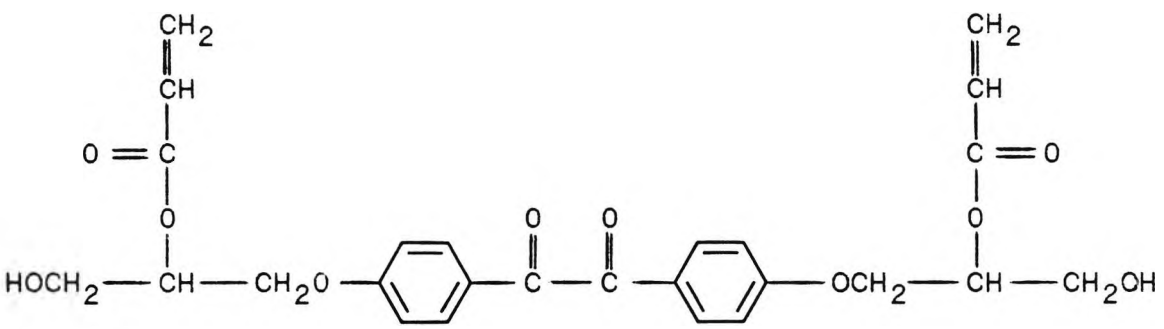
2.78ml (4.08×10^{-2} mol) acrylic acid, 0.20ml (1.30×10^{-3} mol) N,N-dimethylbenzylamine, 8.00×10^{-3}g (3.63×10^{-5} mol) 2,6-di-^{t}butyl-4-methylphenol and 4ml benzene were combined. The resulting mixture was added dropwise to a stirred solution of 4.78g (1.35×10^{-2} mol) benzil-4,4-diglycidyl ether and 4.00×10^{-3}g (1.82×10^{-5} mol) 2,6-di-^{t}butyl-4-methylphenol in 15ml benzene. After heating under reflux for six hours at 85°C, the reaction mixture was cooled to room temperature and diluted with 10ml benzene. The solution was washed with two 25ml portions of ice-cold sodium hydroxide solution and dried over anhydrous sodium sulphate. Solvent evaporation yielded a yellow oil.

Attempts to purify the reaction product in previous preparations led to the formation of unmanageable gums. It was decided, therefore, to use the unpurified material.

It is known that epoxy resins can be modified for UV curing by reaction with (meth)acrylic acid to cause epoxy ring opening[12]. This procedure was applied to the diglycidyl ether prepared as described on p. 241.

NMR Spectrum ($CDCl_3$) : δ 8.10-7.83 (d,4H,J=8Hz; benzoyl); 7.13-6.80 (d,4H,J=8Hz; aryl); 6.40-5.70 (m,6H,2xCH_2=CH-); 4.50-3.80 (m,6H,2x(-CH_2O- & -CHO-); 3.03-2.63 (m,4H,2x$HOCH_2$)

The NMR spectral data is consistent with addition of the acrylate functionality to yield the primary, rather than the secondary, alcohol product.



Primary Alcohol Product

IR Spectrum (NaCl Windows) : 3487 (O-H str.); 3070 (olefinic C-H str.); 3035, (aryl C-H str.); 2933 (alkyl C-H str.), 1726 (ester C=O str.), 1661 (diketone C=O str.), 1597, 1571 & 1507 (aryl C-C str.); 1452 (alkyl C-H str.); 987 & 915 (CH_2=CH- out-of-plane C-H def.); 844 (p-disubstituted aromatic out-of-plane C-H def.); 812 (acrylate C-H def.) cm^{-1}

All reagents were supplied by Aldrich Chemical Company and were used without further purification.

IX : 4,4'-Diacetamidobenzil

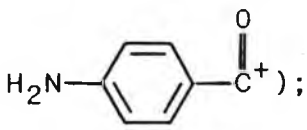
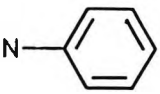
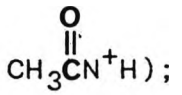
The above-named benzil derivative was produced using a procedure proposed by Gee and Harley-Mason[13].

Procedure

7.5g(0.047 mol) anhydrous copper sulphate, 5ml water and 12.5ml pyridine were heated to give an homogeneous solution. 5.0g (0.015 mol) 4,4'-diacetamidobenzoin were added to the pyridine solution and the resulting mixture was heated to 100°C for two hours, stirring continuously. The hot solution was thenpouredinto cold water, precipitating out a yellow solid. The product was isolated by filtration and recrystallized from acetic acid in 87% yield. Melting range = 248-249°C.

NMR Spectrum (DMSO-d_6) : δ 7.53 (s,8H,aryl); 1.73 (s,6H,2xCH_3-);

IR Spectrum (KBr Disc) : 3350 & 3363 (secondary amide N-H str.); 1705 (ketone C=O str.); 1670 (amide I); 1590 (aryl C-C str.); 1526 (N-H bend); 1370 ($CH_3\overset{O}{\overset{\|}{C}}NH$ C-H str.); 846 (p-disubstituted aromatic out-of-plane C-H def.); cm^{-1}

Mass Spectrum : m/z (int:) : 324 (1.0; M^+) 163 (9.3; $(M_{/2} + H)^+$); 162 (100.0; $M^+_{/2}$); 120 (61.8; ); 92 (15.2; ); 58 (3.8; );

UV Spectrum (DMSO): $n-\pi^*$ λ_{max} = 321nm; $\varepsilon = 6.7 \times 10^4$

4,4'-Diacetamidobenzoin was prepared as described on p. 245 Anhydrous copper sulphate, pyridine and deuterated dimethylsulphoxide were supplied by Aldrich Chemical Company and were used without further purification.

Acetic acid, supplied by BDH, was used without further purification.

X : 4,4'-Diaminobenzil

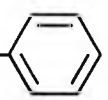
Procedure

4,4'-Diacetamidobenzil was prepared as described above, starting with 10g 4,4'-diacetamidobenzoin. The recrystallized product was boiled for thirty minutes with 50ml concentrated hydrochloric acid, then allowed to cool to room temperature. The yellow solid was isolated by filtering through a No.4 sinter and dissolved in water.

4,4'-Diaminobenzil was precipitated out by adding ammonia solution to the aqueous solution. The product was isolated by filtration and recrystallized from ethanol in 40% yield. Melting range = 166-167°C (literature value[13] 169°C).

NMR Spectrum (Acetone-d_6) : δ 7.71-7.54 (d,4H,J=8Hz; benzoyl); 6.86-6.57 (d,4H,J=8Hz; aryl); 5.46-4.57 (broad s,4H,2x Ar-NH_2);

IR Spectrum (KBr Disc) : 3429, 3343 & 3225 (N-H str.); 3036 (aryl C-H str.); 1630 (ketone C=O str.), 1592 (N-H def.); 1570 & 1510 (aryl C-C str.); 1298 (C-N str.); 840 (p-disubstituted aromatic out-of-plane C-H def.) cm^{-1}

Mass Spectrum : m/z (int:) : 240 (3.2; M^+) 120 (100.0; $M^+/_2$); 92 (33.5; );

UV Spectrum (Ethanol): n-π^* $\varepsilon = 3.5 \times 10^4$; λ_{max} = 348nm

Concentrated hydrochloric acid, ammonia and ethanol were supplied by BDH and were used without further purification. Deuterated acetone was supplied by Aldrich Chemical Company.

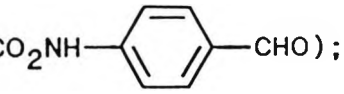
XI : Benzil-4,4'-Bis(n-Butyl Urethane)

Procedure

1.20g sodium hydroxide were dissolved in 6ml water and added to 7.20g (0.03 mol) 4,4'-diaminobenzil in tetrahydrofuran. To this stirred solution were added 4.55g (0.03 mol) n-butyl-chloroformate dropwise. T.L.C. analysis (CH_2Cl_2/MeOH 95:5) showed some starting material to be still present after stirring the reaction mixture at room temperature for several hours. A further 1.20g sodium hydroxide in 6ml water were added, therefore, followed by the dropwise addition of 4.55g n-butylchloroformate. After stirring at room temperature overnight, the organic layer was separated from the aqueous layer and the former was dried over anhydrous sodium sulphate. Solvent evaporation yielded a solid yellow residue, which was recrystallized from ethanol in 45% yield. Product melting range = 193-194°C.

NMR Spectrum (DMSO-d_6) : δ 10.17 (s,2H,2x-NH-); 8.07-7.57 (2d,8H,J=9Hz; aryl), 4.27-4.07 (m,4H,2x-CH_2CO_2-); 1.78-1.15 (m,8H,4x-CH_2-); 1.13-0.71 (m,6H,2x CH_3-);

IR Spectrum (KBr Disc) : 3336 (N-H str.); 3030 (aryl C-H str.), 2934 & 2870 (alkyl C-H str.), 1745 (urethane C=O str.); 1655 (ketone C=O str.); 1581 & 1526 (aryl C-C str.); 852 (p-disubstituted aromatic out-of-plane C-H def.); cm^{-1}.

Mass Spectrum : m/z (int:) : 440 (0.08; M^+); 425 (0.01; $(M-CH_3)^+$); 220 (100.0; $M^+/2$); 164 (28.31; ); 57 (21.62; $CH_3(CH_2)_3^+$);

UV Spectrum (THF): $n-\pi^*$ λ_{max} = 312nm ; ε = 3.5×10^4

4,4'-Diaminobenzil was prepared as described on p. 246. DMSO-d_6, n-butylchloroformate and anhydrous sodium sulphate were supplied by Aldrich Chemical Company. Dichloromethane, methanol, tetrahydrofuran and ethanol were supplied by BDH and were used without further purification.

5.2.2 PREPARATION OF MONOMERIC BENZOIN DERIVATIVES

A number of methods exist by which benzoins can be prepared:-

1) The condensation of two molecules of aromatic aldehyde in the presence of cyanide ion. This method is known as the benzoin condensation.

2) The conversion of an unsymmetrical benzoin into its isomer.

3) The condensation of an aryl glyoxal with an aromatic hydrocarbon.

4) The reaction of an aryl Grignard reagent with a mandelonitrile or a mandelamide.

5) Reduction of a benzil to its corresponding benzoin.

6) Reduction of an aromatic acid or its derivative.

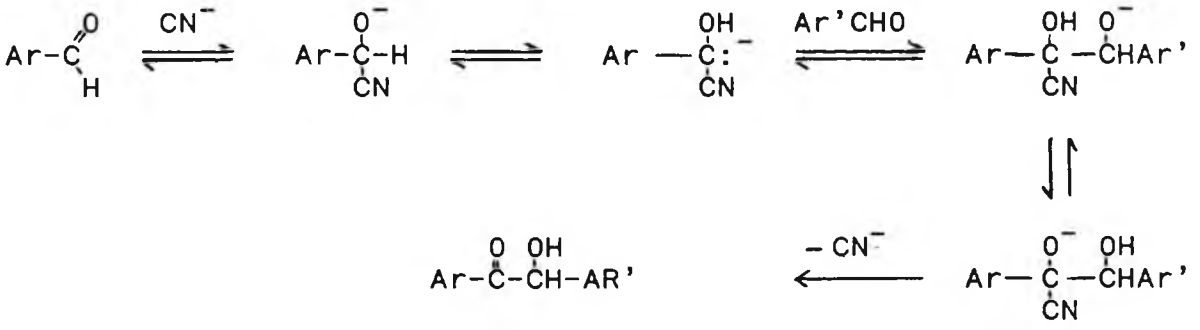
7) The introduction of a hydroxyl group into a desoxybenzoin.

In addition to the seven listed preparative methods, a number of miscellaneous procedures exist which have limited application.

The Benzoin Condensation

The benzoin condensation involves the treatment of an aromatic aldehyde with potassium cyanide or sodium cyanide. The reaction is usually performed in ethanolic solution and, by using one mole of each of two different aromatic aldehydes, unsymmetrical benzoins can be prepared. Mechanistic studies[14] showed the active carbonion

intermediate to be a C-deprotonated cyanohydrin, the proposed reaction mechanism being as follows:

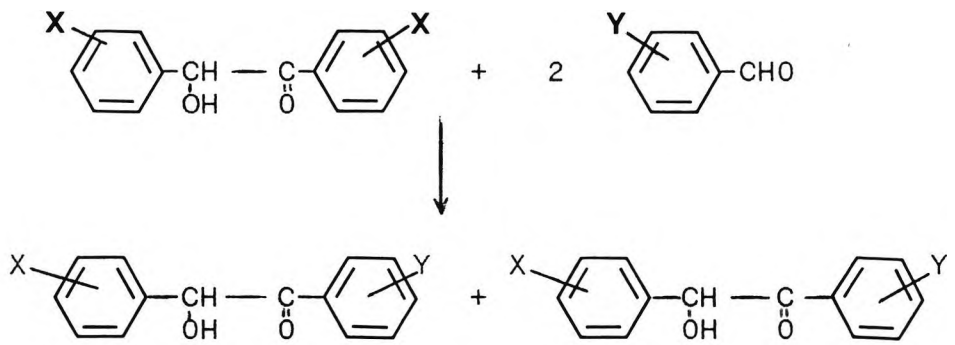


The benzoin condensation is not applicable to all aromatic aldehydes, and no generalization is known by which the types of aromatic aldehydes which will undergo condensation can be predicted. Many aldehydes which will not form symmetrical benzoins can be condensed with other aldehydes to yield unsymmetrical benzoins[7]. For an aromatic aldehyde to be capable of forming a symmetrical benzoin it must possess a labile hydrogen atom in addition to a relatively unsaturated carbonyl group. An unsymmetrical benzoin can be formed from two aldehydes, neither of which will form a symmetrical benzoin,if one aldehyde is a hydrogen donor and the other an acceptor. Whilst it might be expected that two different aldehydes would yield a mixture of two symmetrical and two unsymmetrical benzoins, only a single unsymmetrical product is usually isolated.

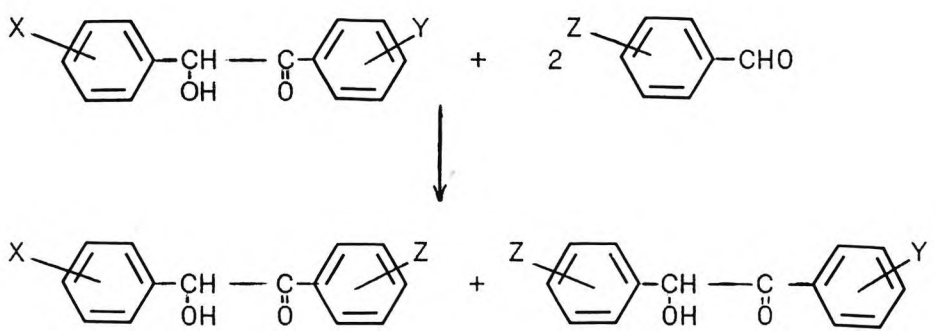
The poor product yields obtained with some benzoin condensations can be attributed to the tendency of benzoin to revert to benzaldehyde in the reaction mixture. Other products, including benzoic acid, benzyl alcohol and ethyl benzoate, are also formed[15,16]. The reversion of benzoin to aldehyde has been used as a means of synthesizing unsymmetrical benzoins[17]. It is possible to obtain a new benzoin by adding two moles of an aldehyde and one mole of a benzoin, or one mole of each of two symmetrical benzoins, to a solution of potassium cyanide in aqueous ethanol[7].

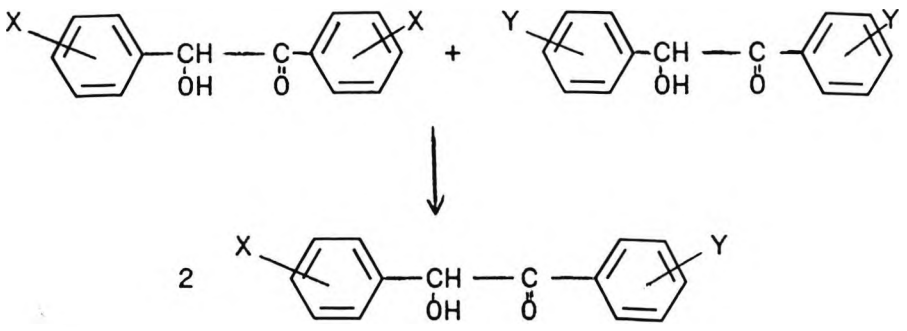
The three types of possible reaction are as follows:

(i)



(ii)



(iii) 

Such interconversions can be effected by the direct addition to the reaction mixture in which a benzoin has been formed of another benzoin or an aldehyde.

The Conversion of an Unsymmetrical Benzoin into Its Isomer

Unsymmetrical benzoins may exist in either of two isomeric structures, differing in the relative positions of the carbonyl and carbinol groups:



One isomer is, generally, more stable than the other and the less stable will isomerize under relatively mild conditions to the more stable form. The more stable isomer can also be converted into the less stable form by indirect means. Isomeric interconversion can be useful for the preparation of certain benzoins which are difficult to obtain by one of the

standard preparative methods. Several examples of interconversions have been recorded[12,18-23].

The Condensation of Arylglyoxals with Aromatic Hydrocarbons

The condensation of phenylglyoxals with aromatic hydrocarbons in the presence of aluminium chloride affords benzoins in 35-90% yield[24-26]. Equal success has been achieved with substituted or unsubstituted phenylglyoxals and substituted or unsubstituted aromatic hydrocarbons. The method has been found to be particularly useful for halogen- and methyl-substituted benzoins[7]. It is not, however, applicable to the condensation of highly hindered arylglyoxals with certain highly substituted aromatic compounds to form unsymmetrical benzoins. For example, mesitylglyoxal condenses with 1,3,5-triethylbenzene to yield a diarylbenzoyl methane instead of a benzoin.

$$2,4,6\text{-}(CH_3)_3\ C_6H_2COCHO + 1,3,5\text{-}(C_2H_5)_3\ C_6H_3$$

$$\downarrow\ AlCl_3$$

$$2,4,6\text{-}(CH_3)_3\ C_6H_2COCH\ [C_6H_2(C_2H_5)_3\text{-}2,4,6]_2$$

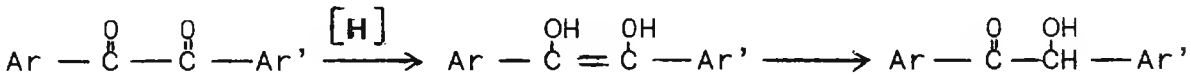
The Reaction of Grignard Reagents with Mandelamides and Mandelonitriles

Aromatic magnesium halides react with mandelamides and mandelonitriles to form both symmetrical and unsymmetrical benzoins. Whilst the yields are relative low (typically 20-47%) and the experimental procedures time-consuming, this method has been found to be the best route to a number of benzoins[27-32].

Symmetrical amd unsymmetrical methyl and halogen-substituted benzoins have been synthesized in addition to the less stable isomers of unsymmetrical benzoins.

The Reduction of Benzils

One serious limitation of this method of forming benzoins is that the majority of benzils are, in fact, produced by oxidation of the corresponding benzoins. In the absence of specific catalysts the mechanism of benzil reduction is probably initial 1,4-addition of hydrogen, followed by rearrangement of the enediol intermediate.



The formation of other reduction products in addition to, or in place of, the benzoin is dependent upon the reagents and conditions employed. Other possible products of reduction are:

$$Ar\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ar',\ Ar\text{-}CH_2\text{-}CH_2\text{-}Ar',\ Ar\text{-}CH(OH)\text{-}CH(OH)\text{-}Ar'$$

$$\text{and } Ar\text{-}CH_2\text{-}CH(OH)\text{-}Ar'$$

Since the two carbonyl groups of unsymmetrical benzils generally possess very different reactivities, it is usual for only one of them to be reduced. The stable isomeric form of the corresponding benzoin will thus be produced[33,34].

The Reduction of Aromatic Acids and Derivatives

Aromatic acids, their chlorides, esters and peroxides can be reduced by treatment with magnesium and magnesium iodide in a benzene/ether solvent mixture[35,36].

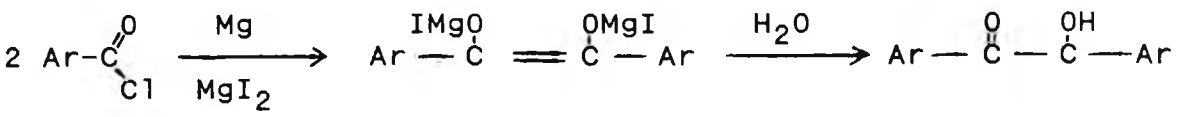
With benzoic acids or benzoyl peroxides, the reaction takes place in two stages:

(i) displacement of the acid hydrogen by MgI;

and

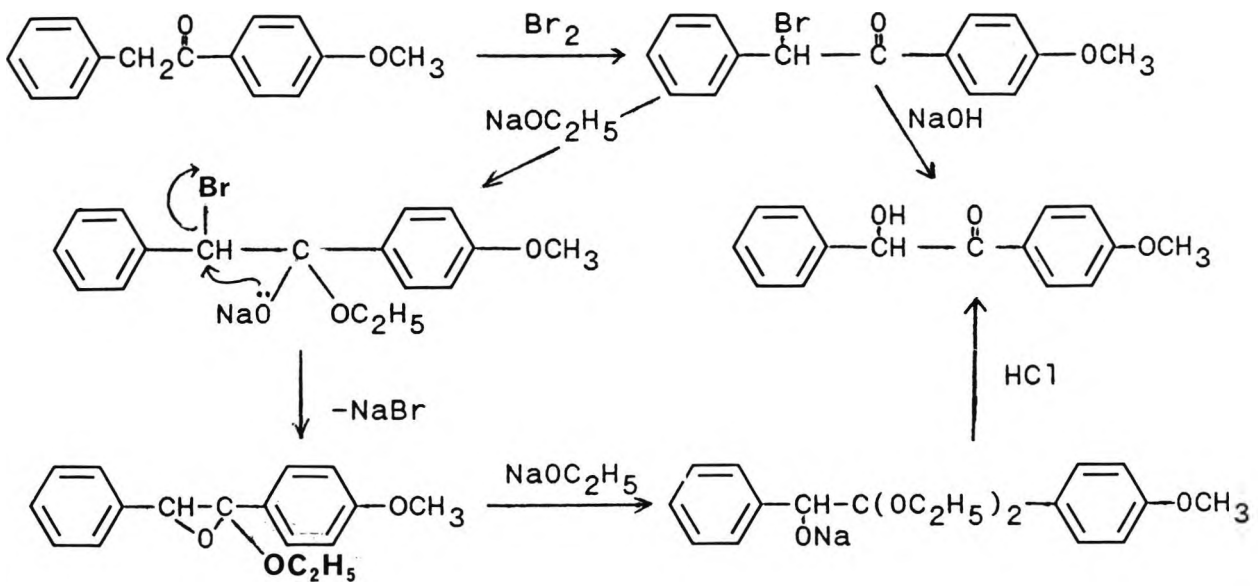
(ii) reduction of the resulting salt.

With acid chlorides and esters, the magnesium iodide derivative of the enediol is formed directly and is hydrolyzed to the benzoin[7].



The Conversion of Desoxybenzoins into Benzoins

Since desoxybenzoins possess an α-hydrogen atom which is readily displaced, these materials can serve as starting materials for the preparation of benzoins. Under the influence of light, bromine will convert a desoxybenzoin into an α-bromodesoxybenzoin [28,37]. The reaction of α-bromodesoxybenzoins with alkali forms benzoins[28,37,38], whilst their reaction with sodium ethoxide yields ketals. These ketals are readily hydrolyzed with cold dilute mineral acid to the corresponding benzoins.

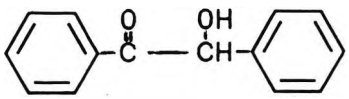


Miscellaneous Methods of Benzoin Synthesis

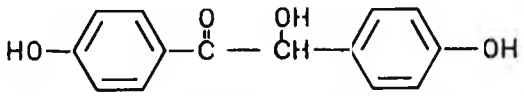
Small amounts of benzoin have been isolated (usually as by-products) from a variety of reactions[39-42]. Other procedures have afforded certain benzoins in varying yields. For example, α-hydroxydiphenylacetaldehyde undergoes rearrangement in acidic ethanol to benzoin in addition to a small quantity of the benzoin ethyl ether[43]. 1,3-Diphenyl-1,2,3-propanetrione, on treatment with phenylmagnesium bromide or phosphoric acid in acetic acid, undergoes rearrangement to yield benzoin[24,44,45]. 1-Methyl-anthraquinone can be oxidized with manganese dioxide to yield the corresponding benzoin directly[46].

None of these miscellaneous methods have been studied in depth for the synthesis of benzoins, and data regarding the yields afforded is scarce.

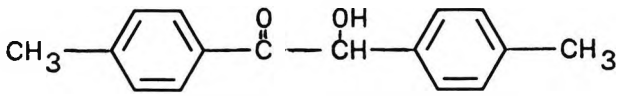
Monomeric Benzoin Derivatives



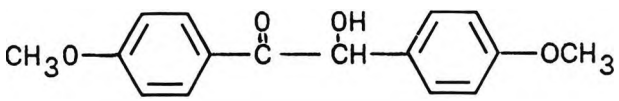
Benzoin
XII



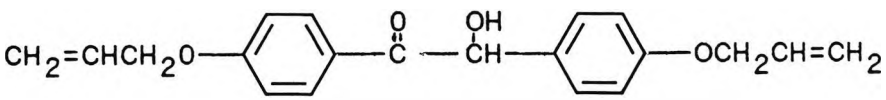
4,4'-Dihydroxybenzoin
XIII



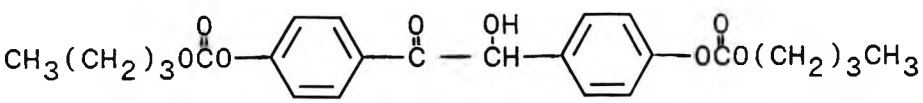
4,4'-Dimethylbenzoin
XIV



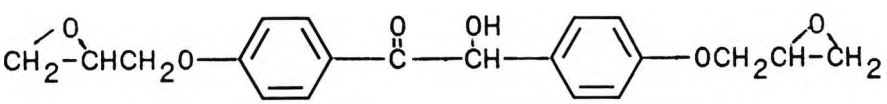
4,4'-Dimethoxybenzoin
XV



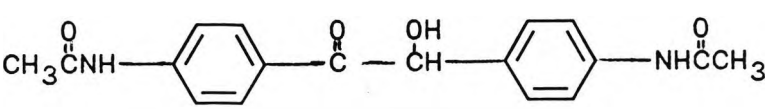
Benzoin-4,4'-Diallyloxy Ether
XVI



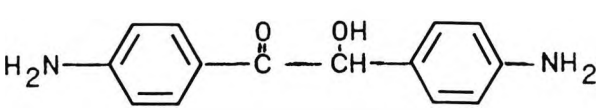
Benzoin-4,4'-Bis(n-Butyl Carbonate)
XVII



Benzoin-4,4'-Diglycidyl Ether
XVIII



4,4'-Diacetamidobenzoin
XIX



4.4'-Diaminobenzoin
XX

Since preparative routes to the corresponding benzils had been found, it was attempted to produce the majority of the desired benzoin derivatives by reduction of their benzil analogues. In a few cases benzoin condensations were attempted.

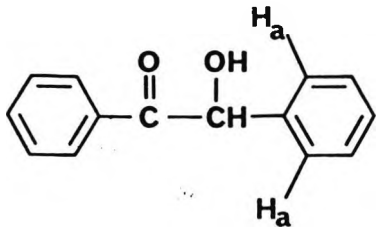
XII: Benzoin

Benzoin was obtained via a symmetrical benzoin condensation with benzaldehyde, following the procedure described by Vogel[47].

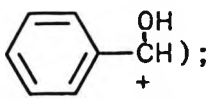
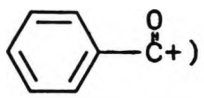
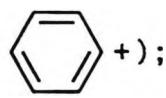
Procedure

5.0g (0.047 mol) benzaldehyde , 6.5ml ethanol and a solution of 0.5g (0.010 mol) sodium cyanide in 5.0ml water were heated under reflux for 30 mins. The reaction mixture was cooled in an ice bath and the crystalline product was isolated by filtration. Recrystallization from ethanol afforded pale yellow needles in 80% yield, melting range = 137-138°C.

NMR Spectrum (DMSO-d_6): δ 8.00-7.74 (m,2H,2xH_a); 7.60-7.07 (m,8H,aryl protons, 6.01-5.76 (m,1H,-CH-); 4.64-4.30 (m,1H,-OH)



IR Spectrum (KBr Disc): 3417 (hydroxyl O-H str.); 3083, 3059 & 3028 (aryl C-H str.); 2932 (alkyl C-H str.); 1677 (ketone C=O str.), 1594, 1575, 1488 & 1448 (aryl C-C str.); 1317 (alkyl C-H def.), 755 & 705 (monosubstituted aromatic C-H def.) cm^{-1}

Mass Spectrum : m/z (int.): 212 (0.7; M^+); 211 (0.2; $(M-1)^+$); 107(5.7; );105(100.0; );77(61.5; );

UV Spectrum (DMF): $n - \pi^*$ $\varepsilon = 258$; $\lambda_{max} = 326nm$

XIII 4,4'-Dihydroxybenzoin

If a symmetrical benzoin condensation could be effected with O-protected 4-hydroxy benzaldehyde, this would afford 4,4'-dihydroxy benzoin on removal of the protecting groups. Protection of the hydroxyl function with the tetrahydropyran group (achieved by reacting the hydroxyl with 2,3-dihydropyran) afforded a viscous liquid. Attempting to purify this liquid by Kugel distillation resulted in opening of the tetrahydropyran ring, as indicated by NMR spectral analysis. In order to overcome this problem, protection of

the hydroxyl function was repeated and a benzoin condensation was repeated in situ, without attempts at prior purification. This, however, failed to yield the desired product, with unreacted aldehyde being recovered after refluxing for several days in the presence of sodium cyanide in aqueous ethanol.

The hydroxyl function of 4-hydroxybenzaldehyde was then protected as an allyl ether (achieved by reaction with allyl bromide and anhydrous potassium carbonate in dry acetone). Attempts to effect the benzoin condensation with this product again failed, unreacted starting material being recovered.

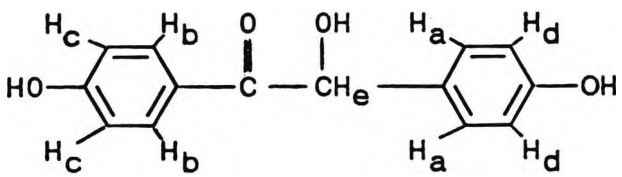
Since attempts to produce 4,4'-dihydroxybenzoin by means of a benzoin condensation had failed it was decided to attempt the reduction of 4,4'-dihydroxybenzil. 4,4'-dihydroxybenzil was prepared as described on p.235 and was reduced according to the procedure reported by Backeberg and van Es[48].

Procedure

2.37g (9.80×10^{-3} mol) 4,4'-dihydroxybenzil, 7.5g sodium dithionite, 75ml ethanol and 75ml water were heated under reflux for 30 mins. The majority of the solvent was removed

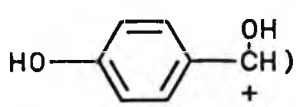
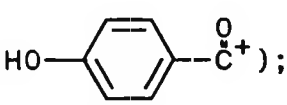
in vacuo and the mixture allowed to cool to room temperature. The crystalline product which separated out was isolated by filtration and recrystallized twice from ethanol in 65% yield. Melting range = 197-198°C.

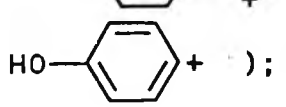
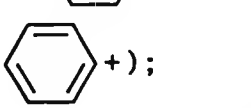
NMR Spectrum (Acetone-d_6): 9.10-8.30 (broad s,2H,2 x Ar - OH); 8.07-7.90 (d,2H,J=9Hz ; H_a); 7.37-7.10 (d,2H,J=9Hz ; H_b); 7.00-6.75 (m,4H,H_c & H_d) ; 5.97 (s,1H, H_e) ;



IR Spectrum (KBR Disc): 3494 & 3326 (H-bonded hydroxyl O-H str.); 3133 (intramolecularly H-bonded hydroxyl O-H str.); 1659 (ketone C=O str.); 1600, 1573 & 1512 (aryl C-C str.); 1271 (O-H bend); 843 & 821 (p-disubstituted aromatic out-of-plane C-H def.) cm^{-1}.

Mass Spectrum : m/z (int.): 244 (1.9; M^+);

123 (100.0; ); 121 (61.6; );

93 (9.6; ); 77 (12.0; );

UV Spectrum (DMSO): $n - \pi^*$ $\varepsilon = 1.47 \times 10^4$; $\lambda_{max} = 281nm$

XIV & XV : 4,4'-Dimethylbenzoin & 4,4'-Dimethoxybenzoin

4,4'-Dimethylbenzoin and 4,4'-dimethoxybenzoin were both supplied by Aldrich Chemical Company and were used without further purification.

XVI : Benzoin-4,4'-Diallyloxy Ether

4-Allyloxybenzaldehyde had already been prepared and a benzoin condensation attempted, when trying to prepare 4,4'-dihydroxybenzoin. This having failed, allylation of the phenyl hydroxyl groups of 4,4'-dihydroxybenzoin was attempted, following the procedure employed to prepare benzil-4,4-diallyloxy ether (see p. 259). The melting range and spectral analyses of the recrystallized product, however, showed that oxidation had taken place simultaneously with allylation. Thus, benzil-4,4'-diallyloxy ether, and not benzoin-4,4'-diallyloxy ether, had been prepared and isolated.

XVII : Benzoin-4,4'-Bis(n-Butyl Carbonate)

Since the corresponding benzil derivative, benzil-4,4'-bis(n-butyl carbonate), had previously been prepared, a reduction with sodium dithionite was attempted, following the

procedure of Backeberg and van Es [48]. Spectral analysis of the crude product afforded by this method indicated that reduction had proceeded through to 4,4'-dihydroxybenzoin.

XVIII : Benzoin-4,4'-Diglycidyl Ether

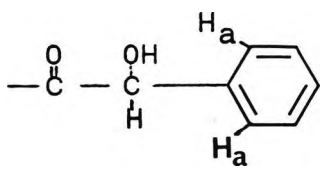
It was hoped that benzoin-4,4'-diglycidyl ether could be produced by the reduction of the corresponding benzil. Several different methods were tried, including refluxing with sodium dithionite in aqueous ethanol; heating with sodium dithionite in 1M sodium hydroxide; and heating with benzpinacol in decalin[49]. The sodium dithionite reductions produced unmanageable gums, whilst spectral analyses of the crystalline product material afforded by the benzpinacol reaction showed it to be clearly not the desired product (product not identified).

Since reductions of the corresponding benzil had failed, it was attempted to produce benzoin-4,4'-diglycidyl ether by the reaction of 4,4'-dihydroxybenzoin with epichlorohydrin. The procedure followed was that used to prepare benzil-4,4'-diglycidyl ether.

Procedure

0.98g (4.02×10^{-3} mol) 4,4'-dihydroxybenzoin and 2.75ml (1.49×10^{-2} mol) epichlorohydrin in 50ml isopropanol were heated to 75°C. 0.35g of 50% sodium hydroxide was added dropwise to the stirred solution and the temperature of the mixture was increased to approximately 83°C. The temperature was maintained at 83°C overnight and a further 2.75ml epichlorohydrin and 0.35g 50% sodium hydroxide were added the following day. The temperature was maintained at 83°C for an additional 48 hours and, since T.L.C. analysis (CH_2Cl_2/MeOH 95:5) showed that the reaction was not progressing further, the mixture was removed from the heat and diluted with water. The product was extracted into ether and conventional work-up afforded a bright yellow oil in 18% yield. Since such a low yield was obtained, purification was not attempted and spectra were recorded for the crude material.

NMR Spectrum ($CDCl_3$) : δ 8.20-7.70 (m,2H,H_a); 7.40-6.68 (m,6H,aryl); 4.37-2.65 (m,10H,2 x CH_2-CHCH_2O -);



IR Spectrum (NaCl windows): 3425 (H-bonded hydroxyl O-H str .); 3070 (epoxide C-H str.); 2969, 2931 & 2879 (alkyl C-H str .); 1670 (ketone C=O str.); 1598, 1571 & 1508 (aryl C-C str.); 1309 (secondary alcohol C-O str.); 1258 (epoxide C-O str.); 1166 (ether C-O str.); 913 (epoxide C-O str.); 843 (p-disubstituted aromatic out-of-plane C-H def.) cm^{-1}.

Whilst the spectral data recorded above appears to indicate that benzoin-4,4'-diglycidyl ether had been produced, all attempts to repeat the above procedure on a larger scale proved unsuccessful. An insufficient amount of product was available for further investigations to be carried out, and the low yields afforded by this method ruled out its suitability as a means of producing benzoin-4,4'-diglycidyl ether.

XIX : 4.4'-Diacetamidobenzoin

4,4'-Diacetamidobenzoin was prepared by a symmetrical benzoin condensation of 4-acetomidobenzaldehyde, as proposed by Gee and Harley-Mason[13].

Procedure

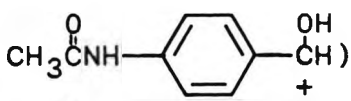
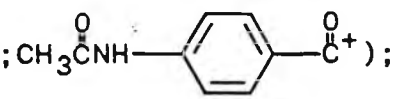
10.0g (0.061 mol) p-acetamidobenzaldehyde, 1.0g (0.015 mol)

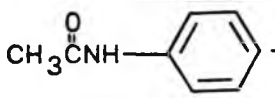
potassium cyanide and 30ml ethanol were heated under reflux for 2 hours. The solution was then diluted with water and allowed to cool to room temperature. The product which precipitated out was isolated by filtration and recrystallized from acetic acid. Drying over potassium hydroxide pellets in a vacuum dessicator afforded a 46% product yield, melting range = 243-245°C (literature value[13] 244-246°C).

<u>NMR Spectrum</u> (DMSO-d_6): δ 10.10-9.77 (2s,2H,2x-NH-) 7.97-7.13 (m,8H,aryl); 5.93 (s,1H,-CH-); 2.05-2.00 (d,6H,J=3Hz;2xCH_3-);

<u>IR Spectrum</u> (KBr Disc.): 3301 & 3270 (secondary amide N-H str.); 1670 (amide and ketone C=O str.); 1594 (aryl C-C str.); 1529 (secondary amide N-H def.); 1410 & 1371 (alkyl C-H def.); 1262 (O-H bend); 1082 (secondary alcohol C-O str./O-H def.); 851 & 821 (p-disubstituted aromatic out-of-plane C-H defs.) cm^{-1}.

<u>Mass Spectrum</u>: m/z (int.); 326 (3.1; M^+); 309 (4.1; $(M-OH)^+$);

164 (100.0; );162 (71.2; );

135 (71.2; );

<u>UV Spectrum</u> : (DMSO): n - π^* ε = 2.0 x 10^4; λ_{max} = 299nm.

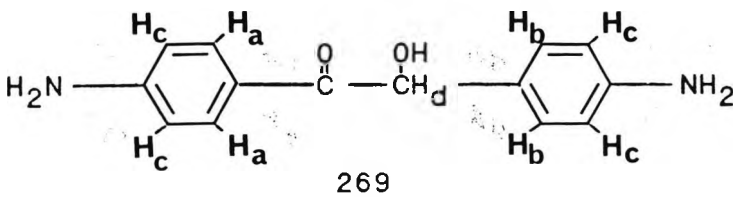
XX : 4,4'-Diaminobenzoin

It was attempted to produce 4,4'-diaminobenzoin by reduction of the corresponding benzil, which was prepared as described on p. 259.

Procedure

1.0g (4.0×10^{-3} mol) 4,4'-diaminobenzil, 3.2g sodium dithionite, 32ml water and 32ml ethanol were heated under reflux overnight. A further 3.2g sodium dithionite and 25ml ethanol were added, and heating under reflux was continued until T.L.C. analysis (CH_2Cl_2/MeOH 95:5) showed all the starting material to have been consumed. The majority of the solvent was removed *in vacuo* and the solution allowed to cool to room temperature. This resulted in the formation of a solid precipitate, which was isolated by filtration and recrystallized from ethanol in 30% yield. Melting range = 172-173°C (literature value[50] 169°C).

NMR Spectrum (Acetone-d_6): δ 7.72-7.69 (m,2H,H_b); 7.13-7.07 (m,2H,H_a); 6.79-6.53 (m,4H,H_c); 6.23 (s,1H,H_d); 5.48-4.66 (s,4H,2x Ar-NH_2); 4.3 (s,1H,-OH);



IR Spectrum (kBr Disc) : 3448 & 3351 (primary amine N-H str.); 3236 (H-bonded hydroxyl O-H str.); 3035 (aryl C-H str.) 1630 (ketone C=O str.); 1593 (aryl C-C str.); 1553 (primary amine N-H bend); 1515 (aryl C-C str.); 1309 (alkyl C-H def.); 1284 (secondary alcohol C-O str.); 857 & 832 (p-disubstituted aromatic out-of-plane C-H def's) cm^{-1}

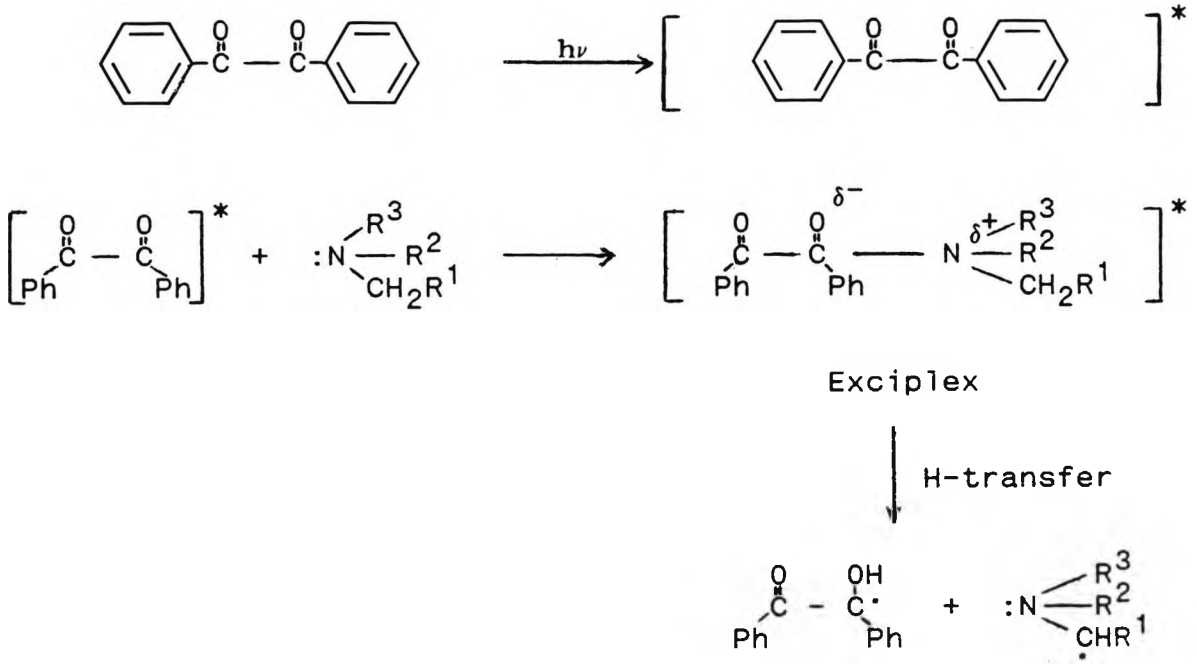
UV Spectrum (Acetone): $n - \pi^*$ $\varepsilon = 1.76 \times 10^4$; λ_{max} = 328nm

5.2.3 SCREENING OF PHOTOINITIATORS BY UV CURING MEASUREMENTS

The monomeric benzils and benzoins were tested as initiators for the photopolymerization of thin films of tetraethyleneglycol diacrylate (T.E.G.D.A.). The photoinitiators were tested in both the presence and absence of N-methyldiethanolamine.

A hydrogen-donating co-initiator is known to greatly increase the rate of polymerization photoinitiated by benzil[51]. The reason for this is that benzil-type photoinitiators produce initiating radicals by means of a bimolecular reaction, and are generally more reactive with tertiary amines than with other hydrogen donors[52]. The high

reactivity of tertiary amines with hydrogen-abstracting photoinitiators has been attributed to the rapid formation of an excited state complex (exciplex)[53].



Benzoin and its alkyl ethers are known to produce initiating radicals by a unimolecular cleavage mechanism[3,4,54,55]. The presence of N-methyldiethanolamine would not, therefore, be expected to enhance the photoinitiating efficiencies of the benzil derivatives in a similar way to that described above. Nevertheless, tertiary amines have been found to improve the performance of Type I photoinitiators. This effect has been attributed to oxygen scavenging by the amine, reducing the effects of oxygen inhibition[56].

5.2.3.1 **UV Curing of Thin Films**

0.1M solutions of the photoinitiators in T.E.G.D.A. were coated onto strips of G.N.T. paper for curing. A 6 μm wet film thickness was used. When amine was present, a 6:1 N-methyldiethanolamine/photoinitiator molar ratio was employed. For the first set of UV curing measurements the photoinitiator (and amine) concentration was kept constant and the belt speed was varied. Concentration/performance curves were then obtained using a 0.6M amine concentration and fixed belt speed, and varying the concentration of photoinitiator.

N-methyldiethanolamine and tetraethyleneglycol diacrylate were supplied by Aldrich Chemical Company, U.K., and were used without further purification. The UV curing equipment consisted of a moving belt arrangement fitted with two 80W cm^{-1} medium pressure mercury lamps and was supplied by Colordry, U.K. Only one lamp was used to compare the curing efficiencies of the photoinitiators. The substrate onto which the solutions were coated was G.N.T. paper, supplied by Wiggins-Teape, U.K. Wet film thicknesses of 6 μm were obtained with a number 1 K-bar supplied by R.K. Print-Coat Instruments Ltd.

In order to obtain solutions of the benzil and benzoin derivatives in T.E.G.D.A., it was first necessary to dissolve

the photoinitiators in a small amount of an organic solvent. The solutions were then made up to the desired concentration in T.E.G.D.A.

The organic solvents used for the various photoinitiators were as follows:

Photoinitiator	Solvent
I	Acetone
II	Dichloromethane
III	Dichloromethane
IV	Dichloromethane
V	Dichloromethane
VI	Acetone
VII	Chloroform
VIII	Acetone
IX	Dimethylsulphoxide
X	Tetrahydrofuran
XI	Lithium chloride/N,N-dimethylformamide*
XII	N,N-Dimethylformamide
XIII	Tetrahydrofuran
XIV	Tetrahydrofuran
XV	Tetrahydrofuran
XVI	-
XVII	-
XVIII	-
XIX	Dimethylsulphoxide
XX	Acetone

*The lithium chloride/N,N-dimethylformamide mixture consisted of 1g lithium chloride dissolved in 5ml N,N-dimethylformamide. Both were supplied by Aldrich Chemical Company and were used without further purification; similarly for the dimethylsulphoxide and dichloromethane. Acetone,

chloroform and tetrahydrofuran were of general laboratory grade.

5.2.3.2 Monitoring Rates of Cure by Real-Time Infra-red Spectroscopy

In addition to measuring the rate of thin film cure by the number of passes on a moving belt arrangement, the rates of cure achieved with the various photoinitiators were also monitored by real-time infra-red spectroscopy. The curing formulations were coated onto small strips of acetate and were covered with polythene. The films were then exposed to both ultraviolet and infra-red beams, as described in Chapter 3.

Film thicknesses of 24 μm were obtained with a K-bar supplied by R.K. Print-Coat Instruments Ltd. The acetate sheets were supplied by Staedtler of West Germany and the polythene (from household food bags) by Alcan, U.K. Full details of the real-time infra-red spectroscopic apparatus are given on p.159

Rates of cure were monitored in both the presence and absence of N-methyldiethanolamine, the solution compositions being the same as were described earlier in this experimental section. The relative rates were measured and recorded at

0, 3, 6 and 30 secs. after exposure of the samples to the 100W high-pressure mercury lamp (supplied by Osram).

Tetraethyleneglycol diacrylate and N-methyldiethanolamine were supplied by Aldrich Chemical Company and were used without further purification. Spectra were recorded on a Perkin-Elmer 599 infra-red spectrophotometer.

5.3 RESULTS & DISCUSSION

In the results tabulated below, the various photoinitiators are represented by the following numerals:

Photoinitiator	Symbol
Benzil	I
4,4'-Dihydroxybenzil	II
4,4'-Dimethylbenzil	III
4,4'-Dimethoxybenzil	IV
Benzil-4,4'-Diallyoxy Ether	V
Benzil-4,4'-Bis(n-Butyl Carbonate)	VI
Benzil-4,4'-Diglycidyl Ether	VII
4,4'-Bis[(2-Acrylate-3-hydroxy)Propoxy]Benzil	VIII
4,4'-Diacetamidobenzil	IX
4,4'-Diaminobenzil	X
Benzil-4,4'-Bis(n-Butyl Urethane)	XI
Benzoin	XII
4,4'-Dihydroxybenzoin	XIII
4,4'-Dimethylbenzoin	XIV
4,4'-Dimethoxybenzoin	XV
Benzoin-4,4'-Diallyloxy Ether	XVI
Benzoin-4,4'-Bis(n-Butyl Carbonate)	XVII
Benzoin-4,4'-Diglycidyl Ether	XVIII
4,4'-Diacetamidobenzoin	XIX
4,4'-Diaminobenzoin	XX

5.3.1 UV Curing of Thin Films

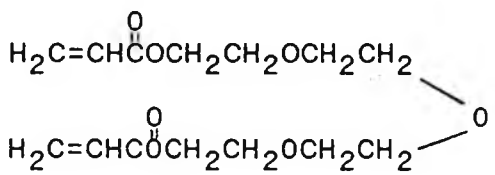
(i) Curing in the Absence of N-Methyl diethanolamine

Photo-initiator	No. of Passes to Cure Film at Given Belt Speed/m min^{-1}									
	14	16	20	21	30	36	43	51	58	72
I	-	-	-	-	-	-	-	-	-	-
II	17	19	26	-	-	-	-	-	-	-
III	-	-	-	-	-	-	-	-	-	-
IV	11	14	15	20	22	30	-	-	-	-
V	13	17	18	27	-	-	-	-	-	-
VI	18	18	21	25	-	-	-	-	-	-
VII	12	12	16	20	26	-	-	-	-	-
VIII	16	17	23	-	-	-	-	-	-	-
IX	19	19	30	-	-	-	-	-	-	-
X	-	-	-	-	-	-	-	-	-	-
XI	26	-	-	-	-	-	-	-	-	-
XII	-	-	-	-	-	-	-	-	-	-
XIII	-	-	-	-	-	-	-	-	-	-
XIV	-	-	-	-	-	-	-	-	-	-
XV	-	-	-	-	-	-	-	-	-	-
XIX	8	8	9	11	14	16	20	21	25	29
XX	-	-	-	-	-	-	-	-	-	-

(ii) Curing in the Presence of N-Methyl diethanolamine

Photo-initiator	No. of Passes to Cure Film at Given Belt Speed/m min^{-1}									
	14	16	20	21	30	36	43	51	58	72
I	8	9	11	12	13	16	20	22	23	25
II	3	4	4	5	7	8	10	13	16	21
III	3	3	5	6	6	7	7	8	9	10
IV	1	1	1	2	2	2	2	3	3	4
V	1	1	1	2	2	2	3	3	4	4
VI	4	5	6	6	7	8	9	10	11	12
VII	1	1	1	1	1	2	2	2	2	2
VIII	1	1	1	1	1	2	2	2	3	3
IX	1	1	2	2	2	2	3	3	4	5
X	4	6	7	8	11	14	18	22	28	30
XI	2	2	2	2	2	2	2	3	3	3
XII	7	8	10	15	19	25	–	–	–	–
XIII	7	7	8	8	9	13	16	19	22	26
XIV	7	8	12	14	15	17	19	25	27	29
XV	2	2	2	4	4	5	6	7	9	10
XIX	2	3	4	4	4	4	5	5	5	5
XX	20	20	21	–	–	–	–	–	–	–
Irgacure 651	4	4	5	5	7	8	9	11	15	17

Since benzil-type photoinitiators produce initiating radicals via hydrogen abstraction from a suitable donor, no cure was expected in the absence of N-methyldiethanolamine. The fact that cure is observed at all with some of the substituted benzils suggests that hydrogen is being donated by either the small quantity of organic solvent used to dissolve the photoinitiators or the T.E.G.D.A. Since neither of these would be expected to donate hydrogen, the most probable explanation is that hydrogen was donated by small traces of water present in the T.E.G.D.A., which is known to be hygroscopic.



Tetraethyleneglycol Diacrylate, T.E.G.D.A.

The substituted benzoins will initiate polymerization by unimolecular cleavage. It would, therefore, be expected that some cure would be obtained with these photoinitiators in the absence of N-methyldiethanolamine. In practise this was not found to be the case, with cure being effected only with 4,4'-diacetamidobenzoin as the photoinitiator under the conditions employed.

As expected, adding N-methyldiethanolamine increased the

rates of cure with all of the photoinitiators. In the case of the substituted benzoins the rate enhancement is attributed to the oxygen-scavenging capacity of the added amine[56].

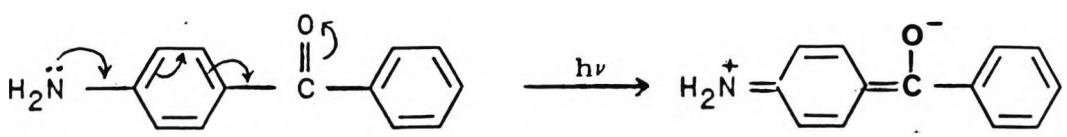
A measure of the efficiencies of the various photoinitiators in the presence of N-methyldiethanolamine was obtained by a comparison with the commercial photoinitiator Irgacure 651. It can be seen that a number of the photoinitiators prepared - including the Type I photoinitiators 4,4'-dimethoxybenzoin and 4,4'-diacetamidobenzoin - effect cure with greater efficiency than Irgacure 651.

The efficiency of a photoinitiator is mainly dependent upon the intensity of light absorption and the rate of deactivation of the excited state. For the 4,4'-disubstituted benzoins, photoinitiating efficiency was found to increase in the order XX < XII < XIV < XIII < XV < XIX. With the exception of XX (4,4'-diaminobenzoin), this corresponds to the order of increasing absorption intensity.

Photoinitiator	UV Solvent	ε
*Benzoin (XII)	N,N-Dimethylformamide	258
4,4'-Dihydroxybenzoin (XIII)	Dimethylsulphoxide	1.5×10^4
*4,4'-Dimethylbenzoin (XIV)	Tetrahydrofuran	420
4,4'-Dimethoxybenzoin (XV)	Tetrahydrofuran	1.9×10^4
4,4'-Diacetamidobenzoin (XIX)	Dimethylsulphoxide	2.0×10^4
4,4'-Diaminobenzoin (XX)	Acetone	1.8×10^4

*Spectra recorded on a Perkin-Elmer Lambda 5 UV/visible spectrophotometer

Benzophenones carrying amino or hydroxyl substituents at the ortho- or para-positions have been found to be surprisingly unreactive in alcoholic solvents. In the case of amino benzophenones, this lack of reactivityhas been attributed to the existence of an intramolecular charge-transfer state, which is assumed to become the lowest energy singlet or triplet state in alcoholic solvents[57].



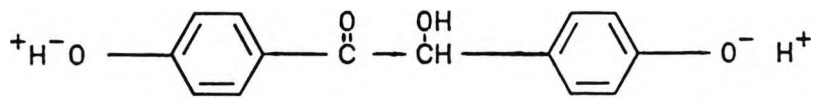
Electron donation to the carbonyl group in the charge-transfer state results in a far lower reactivity than that of an n, π^* state, in which the electrophilicity of the carbonyl oxygen atom is retained. In non-polar solvents, such as cyclohexane, the charge-transfer state is not stabilized and, consequently, the n, π^* state remains the lowest energy state. In polar solvents, in addition to the n, π^* excitation energy being elevated, the energy of the unreactive charge-transfer state is lowered by solvation so that this latter state becomes the lowest energy triplet[58].

It can be assumed that a similar situation exists with 4,4'-diaminobenzoin in acetone, although the polarity of this solvent is much less than that of an alcohol. Thus, the low activity of 4,4'-diaminobenzoin is attributable to the lowest triplet state, under the experimental conditions, being a charge-transfer state.

Considering, now, the Type II photoinitiators, it has been observed that 4-hydroxybenzophenone is not efficiently photo-reduced in alcohols, despite having a lowest n, π^* state[59]. This has been attributed to the pK of excited 4-hydroxybenzophenone, like that of many other phenols, being much larger than that of the ground state. (Promotion of an electron from the oxygen atom of phenol to the ring in an

$n \rightarrow \pi^*$ transition results in a more positive oxygen atom in

( —OH)* and, therefore, greater acidity, i.e. larger pK_a). Consequently, 4-hydroxybenzophenone exists as a phenolate anion, electron donation to the carbonyl group is strong, and photoreduction is difficult. Again, assuming that an analogous situation arises with 4,4'-dihydroxybenzoin, low activity would be expected in polar solvents. However, for the recorded UV curing measurments the photoinitiator was dissolved in non-polar tetrahydrofuran, which would not stabilize the anionic form. Thus, the equilibrium concentration of protonated triplets in the $^3(n, \pi^*)$ states would be of a reasonable level, giving rise to an acceptable efficiency of photoinitiation.



Phenolate form of 4,4'-dihydroxybenzoin in polar solvent.

Similar considerations can be applied to the Type II photoinitiators.

Electronic states are not pure in character; vibronic and spin-orbit coupling result in a mixing of electronic

levels[60,61] so that an n $-\pi^*$ state will possess some $\pi - \pi^*$ character and a $\pi - \pi^*$ state will possess some n $-\pi^*$ character.

In aromatic ketones the energy separation of the S_1 and T_1 states is relatively small (e.g. 25 kJ mol^{-1} in benzophenone compared with 42 kJ mol^{-1} in acetone). Phenyl ketones also possess a second excited $\pi - \pi^*$ triplet state less than 310 kJ mol^{-1} above the ground state[60]. By contributing to the close-lying n $-\pi^*$ triplet, this T_2 state can affect the reactivity of an excited molecule. Furthermore, variation of ketone substituents (and reaction solvents) can often result in an inversion of the n $-\pi^*$ and $\pi - \pi^*$ states. Such an inversion has been observed for some alkoxy substituents; for example, the lowest triplet state of acetophenone is n $-\pi^*$ in character, whilst those of both m-[61] and p-methoxy acetophenone[60] are $\pi - \pi^*$. In preliminary experiments carried out by Hageman[62] it was observed that Type II photoinitiators with $\pi - \pi^*$ lowest excited triplet states exhibit greater photoreactivity than those with lowest n $-\pi^*$ states, when used in combination with tertiary amines. Thus, the higher rates of cure obtained with photoinitiators IV, V, VII & VIII can possibly be explained by their lowest triplet excited state being $\pi - \pi^*$ in character.

In the case of photoinitiator VIII, in addition to a possible $\pi - \pi^*$ lowest triplet excited state, this photoinitiator possesses unsaturated acrylate substituents which are capable of undergoing copolymerization into the polymeric network being formed. Thus, this photoinitiator can be defined as copolymerizable; it has been demonstrated that copolymerizable photoinitiators afford greater efficiency than non-copolymerizable counterparts[63].

5.3.2 Dependence of Cure Rates on Photoinitiator Concentrations

Concentration/performance curves were also obtained for a few of the more efficient photoinitiators and for the commercial Type I photoinitiator Irgacure 651. 0.6M solutions of N-methyldiethanolamine in T.E.G.D.A. with varing photoinitiator concentrations were cured at a belt speed of 30m min^{-1}. For each solution, the number of passes required to cure the 6μm films was noted.

Photoinitiator	Photoinitiator Concentration/M	No. of Passes to Cure Film
Irgacure 651	0.05	10
	0.10	7
	0.15	5
	0.20	5
	0.25	4
	0.30	4
	0.40	4
V	0.05	3
	0.10	2
	0.15	2
	0.20	2
	0.25	2
	0.30	2
	0.40	2
VII	0.05	2
	0.10	2
	0.15	1
	0.20	1
	0.25	1
	0.30	1
	0.40	1
IX	0.05	2
	0.10	2
	0.15	2
	0.20	3
	0.25	3
	0.30	3
	0.40	3
XI	0.05	2
	0.10	2
	0.15	2
	0.20	2
	0.25	2
	0.30	3
	0.40	3

/Contd.

Photoinitiator	Photoinitiator Concentration/M	No. of Passes to Cure Film
XIII	0.05	-
	0.10	9
	0.15	9
	0.20	8
	0.25	5
	0.30	5
	0.40	5
XIX	0.05	5
	0.10	4
	0.15	3
	0.20	3
	0.25	3
	0.30	2
	0.40	Solution polymerized before curing

As expected, the majority of the formulations showed an increase in curing rate with increasing photoinitiator concentration. However, with 4,4'-diacetamidobenzil and benzil-4,4-bis(n-butyl urethane) the rate of cure remained effectively constant with the first few photoinitiator concentrations before decreasing slightly. This slight decrease occurred between the concentrations of 0.15 and 0.20M for 4,4'-diacetamidobenzil and between 0.25 and 0.30M for benzil-4,4'-bis(n-butyl urethane).

It has been shown that optimum photoinitiator

concentrations exist for UV-curable compositions, and that curing performance can decrease upon increasing the photoinitiator concentration beyond this[64]. This was found to occur with 4,4'-diacetamidobenzil and benzil-4,4'-bis(n-butyl urethane).

With all of the other photoinitiators tested - including Irgacure 651 - increasing the photoinitiator concentration beyond the optimum value had no effect upon the rate of cure. The observed effect would appear to be simply a property of the individual photoinitiators.

5.3.3 Monitoring Rates of Cure by Real-Time Infra-red Spectroscopy

Photo-initiating System	Relative Rate of Polymerization at Time t(secs) After Exposure to UV Radiation				Induction Period (secs)
	t = 0	3	6	30	
I	0.33	0.28	0.16	0.05	0.00
I & Amine	1.10	0.25	0.23	0.11	0.00
II	0.00	0.09	0.08	0.05	0.60
II & Amine	3.31	0.76	0.30	0.04	0.00
III	0.00	0.21	0.20	0.06	1.20
III & Amine	0.38	0.28	0.11	0.03	0.00
IV	0.57	0.47	0.35	0.10	0.00
IV & Amine	3.50	0.44	0.29	0.02	0.00
V	3.03	0.30	0.13	0.03	0.00
V & Amine	4.98	0.38	0.23	0.03	0.00
VI	0.05	0.80	0.52	0.01	0.00
VI & Amine	0.14	0.36	0.29	0.06	0.00
VII	2.73	0.84	0.67	0.16	0.00
VII & Amine	5.00	0.97	0.76	0.03	0.00
VIII	0.16	0.24	0.15	0.04	0.00
VIII & Amine	4.29	0.64	0.07	0.00	0.00
IX	0.93	0.32	0.25	0.05	0.00
IX & Amine	4.26	0.34	0.34	0.04	0.00
X	0.06	0.53	0.38	0.10	0.00
X & Amine	0.33	0.65	0.19	0.04	0.00

/Contd.

Photo-initiating System	Relative Rate of Polymerization at Time t(secs) After Exposure to UV Radiation				Induction Period (secs)
	t = 0	3	6	30	
XI	0.12	0.57	0.80	0.05	0.00
XI & Amine	4.62	0.30	0.14	0.07	0.00
XII	0.14	2.73	0.05	0.02	0.00
XII & Amine	1.24	1.85	0.26	0.04	0.00
XIII	2.75	0.39	0.21	0.06	0.00
XIII & Amine	0.69	0.74	0.36	0.03	0.00
XIV	1.99	0.22	0.22	0.00	0.00
XIV & Amine	0.68	6.05	0.36	0.03	0.00
XV	4.23	0.77	0.28	0.20	0.00
XV & Amine	3.49	0.47	0.18	0.01	0.00
XIX	3.21	0.83	0.36	0.03	0.00
XIX & Amine	1.62	0.64	0.26	0.02	0.00
XX	0.00	0.00	0.00	0.00	-
XX & Amine	0.00	0.04	0.04	0.05	2.34
Irgacure 651	0.00	0.03	0.05	0.00	0.00
Irgacure 651 & Amine	12.00	0.29	0.02	0.00	0.00

Induction periods were observed with only three of the photoinitiating systems tested: 4,4'-dihydroxybenzil and 4,4'-dimethylbenzil, both in the absence of a tertiary amine, and 4,4'-diaminobenzoin with amine. No polymerization of the acrylate double bonds was observed throughout the 30 seconds with 4,4'-diaminobenzoin in the absence of amine. Low rates of polymerization were expected for the substituted benzils in the absence of a hydrogen donor, since these photoinitiators operate via a hydrogen-abstraction mechanism. However, the thin film curing measurements obtained earlier had indicated that benzil and 4,4'-diaminobenzil were less efficient photoinitiators in the presence of N-methyldiethanolamine than 4,4'-dihydroxybenzil and 4,4'-dimethylbenzil. Benzil-4,4'-bis(n-butyl carbonate) also appeared to be less efficient than 4,4'-dimethylbenzil in the thin film curing tests. This discrepancy between the thin film curing and RTIR spectral results must be attributed to the different film thicknesses and substrates used for the two techniques. 4,4'-Diaminobenzoin had already been found to be the poorest of the photoinitiators prepared.

Once curing began, the highest rates of polymerization were found close to the initiation of the process for all of the photoinitiating systems except for 4,4'-diaminobenzoin with N-methyldiethanolamine. With this particular

photoinitiating system the rate of polymerization remained essentially constant throughout the irradiation period.

As polymerization progressed the amount of available photoinitiator diminished and, hence, the rates of polymerization decreased accordingly. Generally, the RTIR spectral results confirm those of the UV curing (belt) tests, with respect to photoinitiating efficiencies.

5.4 SUMMARY

A number of symmetrical, 4,4'-disubstituted benzils and benzoins were prepared and tested as photoinitiators for the UV-initiated curing of vinyl monomers. Benzil and its derivatives generate initiating radicals via a bimolecular mechanism. Consequently, reasonable rates of cure were obtained with these photoinitiators only in the presence of a hydrogen-donating tertiary amine. The benzoin derivatives, on the other hand, were expected to undergo unimolecular cleavage, allowing reasonable cure rates in the absence of a synergist. However, it was found that the presence of a tertiary amine was required to achieve acceptable cure rates with the disubstituted benzoins also. The enhancement of the efficiency of Type I photoinitiators observed upon the addition of a tertiary amine has been attributed to the oxygen-scavenging ability of such amines[65]. Thus the enhanced photoinitiating efficiency is the result of reduced oxygen inhibition. Oxygen inhibition is known to be a highly significant factor in UV curing procedures[66].

With the substituted benzoins it was found that photoinitiating efficiency increased with increased UV absorbance

4,4'-Diacetamidobenzoin and 4,4'-dimethoxybenzoin were found to afford higher rates of cure than the commercial Type I photoinitiator Irgacure 651, presumably due to resonance stabilization effects.

Several of the Type II photoinitiators (i.e. benzil derivatives) were also found to be highly efficient in the presence of N-methyldiethanolamine, most notably benzil-4,4'-diglycidyl ether.

In general, it can be concluded that the presence of electron-donating substituents at the 4- and 4'-positions of benzil and benzoin leads to an enhancement of photoinitiating efficiency. In both cases, the presence of amino substituents leads to a decrease in photoinitiating efficiency.

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CHAPTER VI :

POLYMERIC

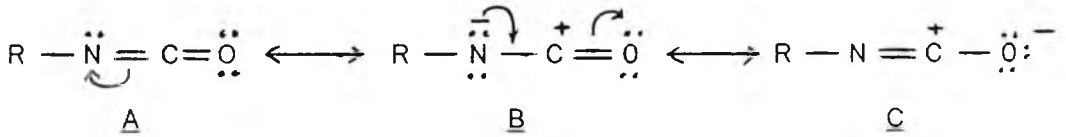
PHOTOINITIATORS

6.1 INTRODUCTION

The monomeric benzils and benzoins prepared as described in the preceding chapter were all 4,4'-disubstituted derivatives. Reaction with suitable disubstituted reagents was, therefore, expected to yield polymeric photoinitiators with the photoreactive moieties incorporated into the polymer backbone.

6.1.1 Advancement of Diols and Diamines with Diisocyanates: Formation of Polyurethanes and Poly(Disubstituted Ureas)

The isocyanate group can be represented by a number of equivalent resonance structures:



A B C

It has been suggested[1] that structure C is the major contributor to the actual configuration of the isocyanate group.

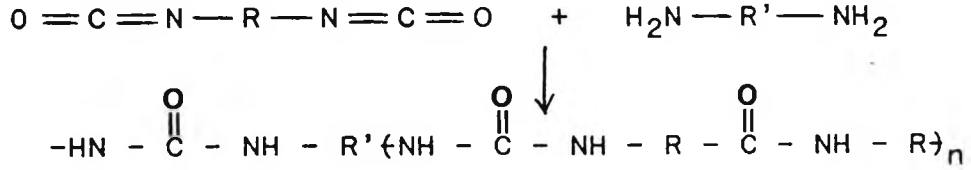
As expected from the high electrophilicity of the carbon atom - which is attached to two electronegative atoms -

isocyanates react readily with compounds possessing active hydrogen atoms. Such reactions involve attack by a nucleophilic centre upon the electrophilic carbon of the isocyanate.

As a direct result of the high reactivity of isocyanates, their reactions are almost invariably accompanied by undesirable side reactions. The reaction of difunctional isocyanates with reagents such as water, amines and alcohols, amongst others, is generally comparable to that of monofunctional isocyanates. Reactions in which polyurethanes and poly(disubstituted ureas) are formed are, therefore, rather difficult to control and repeat .

The reaction of isocyanates with amines is mainly dependent upon the basicity on the N-H bond[1]. In the absence of pronounced steric hindrance, the reactivity of amines towards isocyanates increases with increased amine basicity[3].

The reaction of a primary diamine with a diisocyanate at 0-25°C typically yields a linear poly(disubstituted urea).



Since the poly(disubstituted urea) thus prepared still carries an active hydrogen on each nitrogen, further interaction with unreacted isocyanate is possible, but requires fairly high temperatures[3-5].

The reaction of isocyanates with hydroxylic compounds is one of the most important areas of isocyanate chemistry. Treatment of isocyanates with alcohols results in the formation of substituted urethanes[6]. The effect of steric hindrance in the hydroxyl compound is especially evident for this reaction. At 25-50°C the rate of reaction of secondary alcohols has been found to be 0.3 times that of primary homologues, whilst the reaction of tertiary alcohols is only 0.005 times that of primary alcohols[7].

The reaction of an isocyanate with a phenol occurs considerably more slowly than the reaction with aliphatic alcohols. This is due to the lower nucleophilicity of the phenyl hydroxyl group, phenol being more acidic than aliphatic alcohols. Phenol itself reacts slowly with most isocyanates at 50-75°C[8,9]. As expected, substituents on the phenol nucleus strongly influence the rate of reaction. Electronegative substituents, which further decrease the nucleophilic character of the hydroxyl group, tend to retard urethane formation. For example, 2,4,6-trinitrophenol (picric acid) does not react with isocyanates to give the

urethane, even when subjected to prolonged heating under pressure[10]. The lack of reactivity of the hydroxyl group of 2,4,6-trinitrophenol is attributed to the electronegative influence of the nitro group and to the steric effect of the two ortho-substituents.

The reaction of diisocyanates with diols leads to the formation of polyurethanes[11]. Of the diisocyanates of practical interest, those bearing isocyanate groups of different reactivities are the most versatile. These allow the controlled stepwise synthesis of polymers.

6.1.2 Advancement of Diols and Diamines with Triethyleneglycol Bis(Chloroformate): Formation of Polycarbonates and Polyurethanes

Among the most popular methods used to prepare polycarbonates is the reaction of dihydroxy compounds with phosgene or with bis-chlorocarbonic acid esters of aliphatic dihydroxy compounds[12]. The nature of the end-products formed will be dependent upon the dihydroxy compound used, as well as on the reaction conditions. Phosgene reacts rapidly with aliphatic hydroxyl groups at low temperatures. The reaction of aliphatic chlorocarbonic esters with aliphatic hydroxy compounds proceeds much more slowly, and must be

carried out at elevated temperatures. Aromatic dihydroxy compounds react with phosgene more slowly than do similar aliphatic compounds. Consequently, aromatic polycarbonates cannot be prepared by the direct phosgenation of aromatic dihydroxy compounds. There are four major industrial methods by which aromatic polycarbonates are prepared:

(i) by phosgenation of aromatic dihydroxy compounds in the presence of pyridine;

(ii) by interfacial polycondensation;

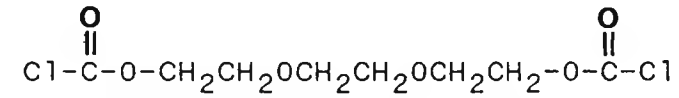
(iii) by isolation of the polycarbonates from their respective solutions;

(iv) by transesterification.

Although there are currently no other methods of commercial significance, numerous additional preparative routes have been reported. Included amongst these are the reaction of carbonic acid diamides with both aliphatic and aromatic hydroxy compounds[13]; transesterification of the diesters of aromatic dihydroxy compounds with diaryl carbonates[14]; and the reaction of dihydroxy compounds, such as 4,4'-dihydroxy-diphenyl - 2,2-propane and 4,4'-dihydroxy-diphenyl-1,

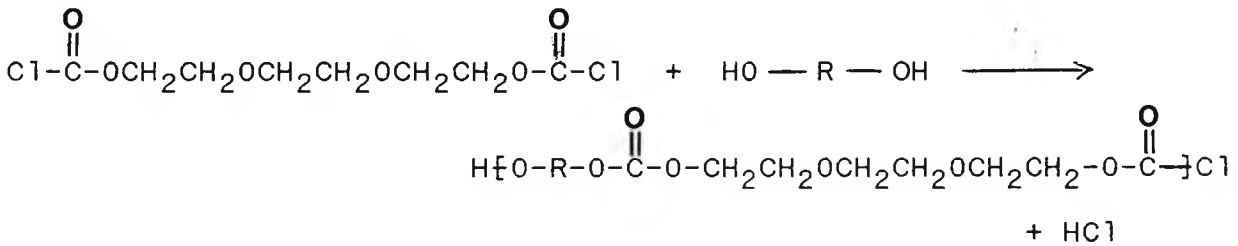
1-cyclohexane, with the bis-chlorocarbonic esters of the same dihydroxy compounds[15].

Triethyleneglycol bis(chloroformate) is a chlorocarbonic acid ester which has recently become commercially available.



Triethyleneglycol Bis(chloroformate)

Reaction of triethyleneglycol bis(chloroformate) with dihydroxy compounds would be expected to afford polycarbonates according to the following equation:



The reaction of di- or poly-functional hydroxy compounds with di- or poly-functional isocyanates is the most widely-used route to polyurethanes. However, there are a number of alternative synthetic routes of lesser importance. The reaction of bis(chloroformates) with diamines - which was first reported in 1945[16] - is one of the most versatile of these alternative routes.

$$Cl-\overset{O}{\overset{\|}{C}}O-R-O\overset{O}{\overset{\|}{C}}-Cl \quad + \quad H_2N-R'-NH_2 \longrightarrow \left(\overset{O}{\overset{\|}{C}}O-R-O-\overset{O}{\overset{\|}{C}}NH-R'-NH\right)_n$$

This method is often applied via 'interfacial polycondensation', which is based upon the formation of a polymer at the interface of two liquid phases, each of which contains one of the reactants. Many investigations have been carried out into the synthesis of polyurethanes by interfacial condensation[17-22].

6.1.3 Advancement of Epoxides with 5,5-Dimethylhydantoin

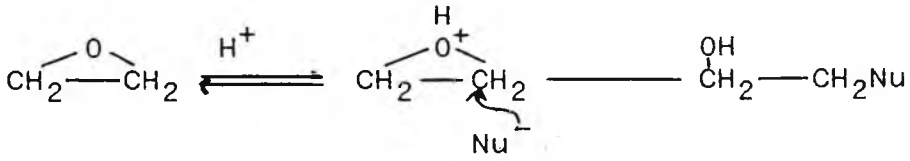
In Lewis terminology, the ether linkage is characteristically both strong and basic. When the ether linkage is within an epoxide ring, however, carbon-oxygen bond cleavage occurs readily in order to overcome the ring strain. Epoxides are cleaved by nucleophiles in the presence of either acid or base, to give rise to a lower-energy, more stable product.

In basic media epoxides undergo S_N2 attack by strong nucleophiles such as the hydroxide ion or alkoxides.

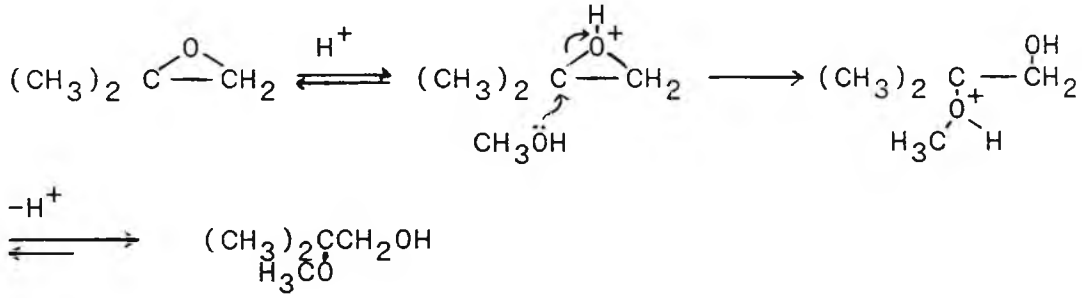
$$RCH\overset{O}{\diagup\!\!\!\!\diagdown}CH_2 + {}^{-}OCH_3 \xrightarrow{S_N2} R\overset{O^-}{\overset{|}{C}}H-CH_2OCH_3 \underset{\longleftarrow}{\xrightarrow{\text{Excess } CH_3OH}} R\overset{OH}{\overset{|}{C}}H-CH_2OCH_3 + CH_3O^-$$

As illustrated above, base-catalyzed cleavage involves nucleophilic attack at the less-hindered carbon.

In acidic media the epoxide oxygen atom is protonated. Protonated epoxides are cleaved even more easily than their non-protonated counterparts, and can be attacked by weak nucleophiles such as water, alcohols and halide ions.



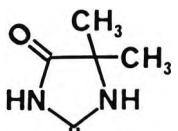
In contrast to base-catalyzed cleavage, attack in acidic media occurs at the more hindered carbon, when the epoxide is unsymmetrical. In this way the most stable carbocation is formed.



The attack of nucleophiles at the more hindered carbon in acidic media has been attributed to the protonated epoxide possessing a reasonable degree of carbocationic character[23]. Since carbocation stability increases with substitution (i.e. tertiary > secondary > primary), the partial positive charge

of the protonated epoxide will be placed on the most substituted carbon atom. This is then the subject of subsequent nucleophilic attack.

Ammonia and amines react with epoxides to yield β-hydroxy-amines[24]. 5,5-Dimethylhydantoin is a difunctional secondary amine which will form polymeric products by reaction with a difunctional epoxy reagent. Copolymers of 5,5-dimethylhydantoin with the diglycidyl ethers of aromatic 4,4-dihydroxy compounds have been previously prepared and investigated[25]. Experimental methods described in this chapter were based upon these preparative procedures.



5,5-Dimethylhydantoin

6.2 EXPERIMENTAL

6.2.1 MATERIALS AND INSTRUMENTATION

Unless otherwise stated, all reagents (apart from those prepared as described in previous chapters) were supplied by Aldrich Chemical Company Ltd. and were used without further purification.

The following abbreviations are used for solvents for analytical purposes:

Solvent	Abbreviation
Dimethylsulphoxide (deuterated)	DMSO-d_6
N,N-Dimethylformamide	DMF
Deuterated Chloroform	$CDCl_3$
Dichloromethane	CH_2Cl_2
Methanol	MeOH

NMR spectra were recorded on a JEOL JNM-PMX 60 S.I. spectrometer, using tetramethylsilane as internal standard. IR spectra were recorded on a Perkin-Elmer 983 G infra-red spectrophotometer.

UV spectra were recorded on a Philips' PU 8720 UV/visible scanning spectrophotometer.

Melting points were determined by means of a Griffin P1158 melting point apparatus.

The UV curing measurements were performed with a Colordry unit, consisting of two 80W cm^{-2} medium pressure mercury lamps over a moving belt arrangement. Only one of the two lamps was used to cure the films. The solutions were coated onto strips of G.N.T. paper, supplied by Wiggins Teape, U.K. Wet film thicknesses of the specified magnitude were obtained by the use of K-bars supplied by R.K. Print-Coat Instruments. Extent of cure was determined by rubbing the surface of the films with a rubber teat; a film was defined as being cured when this failed to leave a visible trail. The real-time infra-red (RTIR) spectroscopic apparatus is illustrated on p. 160 . The UV source was a high pressure mercury lamp supplied by Osram (Osram HBO 100 W/2). Spectra were recorded on a Perkin-Elmer 599 infra-red spectrophotometer.

For the RTIR spectral analyses, films of 24 m thickness were coated onto acetate strips (acetate sheets supplied by Staedtler of West Germany) and were covered with polyethene (from food bags supplied by Alcan, U.K.). Cure kinetics were obtained with the spectrophotometer in time drive mode and

locked onto the 810 cm^{-1} acrylate absorption peak.

The UV curing and RTIR techniques are described in greater detail in Chapter III of this thesis.

6.2.2 ADVANCEMENT OF MONOMERIC BENZILS & BENZOINS TO POLYMERIC SYSTEMS

6.2.2.1 Advancement of 4,4'-Dihydroxybenzil with 1,6-Di-isocyanatohexane

Procedure I

2.42g (0.01 mol) 4,4'-dihydroxybenzil were added to a stirred solution of 1.68g (0.01 mol) 1,6-diisocyanatohexane in 16ml N,N-dimethylformamide. T.L.C. analysis showed that some unreacted starting material still remained after stirring at room temperature for one hour. Consequently the solution was warmed to 60°C for several hours. On cooling the solution to room temperature a solid precipitate was formed. The precipitate was isolated by filtration and washed with cold ethanol. The solid product was found to be very sparingly soluble in dimethylsulphoxide and insoluble in all other common laboratory solvents. No melting was observed up to 300°C.

Procedure II

It was hoped that ethanol added to the reaction mixture would function as a chain transfer agent, limiting the molecular weight of the polyurethane formed. A slightly lower proportion of the diisocyanate was used also, and the reaction mixture was kept at ambient temperature throughout.

2.42g (0.01 mol) 4,4'-dihydroxybenzil were dissolved in a small amount of N,N-dimethylformamide. The dihydroxybenzil solution was added to a stirred solution of 2.90g (9.00×10^{-3} mol) 1,6-diisocyanatohexane and 1ml enthanol in 10ml N,N-dimethylformamide. Stirring was continued for approximately three hours before leaving the mixture to stand for a few hours. Precipitation of the solid which thus began to form was hastened by the addition of ethanol. The product was isolated by filtration and dried for several hours in a vacuum oven at approximately 30°C. Product yield = 85%, melting range = 172-174°C.

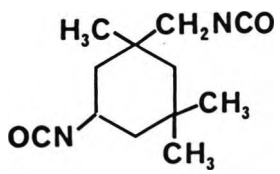
NMR Spectrum ($DMSO-d_6$): δ 8.11-7.78 (m,4H,benzoyl); 7.47-7.17 (m,4H,aryl); 3.20-2.88 (m,4H,2x($-CH_2-N-$)); 1.67-0.93 (m,8H, 4 x $-C-CH_2-C-$);

IR Spectrum (KBr Disc): 3324 (-N-H str.); 2930 & 2857 (alkyl C-H str.); 1708 (urethane C=O str.); 1669 (ketone C=O str.);

1600 (aryl C-H str.); 1529 (urethane C=O str./O-H def.); 1497 (aryl C-H str.); 860 (p-disubstituted aromatic out-of-plane C-H def) cm^{-1}.

UV Spectrum (DMF): λ_{max} = 273 nm; photoreactive group content = 40%.

6.2.2.2 Advancement of 4,4'-Dihydroxybenzil with Isophorone Diisocyanate



Isophorone Diisocyanate

It was hoped that the somewhat unusual structure of isophorone-diisocyanate would prevent regular packing in the polymeric product formed. This should afford better solubility properties than were obtained with the polyurethanes from 1,6-diisocyanatohexane. A few procedures were attempted and the one recorded as follows was found to be the most successful.

Procedure

4.00g (0.018 mol) isophorone diisocyanate, 0.19g (0.002 mol)

phenol and 20ml N,N-dimethylformamide were combined in a flask. To this mixture was added a solution of 4.84g (0.020 mol) 4,4'-dihydroxybenzil in 5ml N,N-dimethylformamide. The combined solutions were stirred at room temperature for five hours, then poured into cold water. The product was isolated by extracting three times with ether. The ether extracts were combined, washed once with water and dried over anhydrous sodium sulphate. Solvent evaporation in vacuo yielded a viscous yellow oil, which afforded a crystalline solid when dried on a vacuum pump. Product yield = 18%.

NMR Spectrum ($CDCl_3$): δ 7.95-7.73 (m,4H,benzoyl); 7.00-6.67 (m,4H aryl),4.27-3.90 (q,2H,$-CH_2N-$); 1.33-0.93 (m,15H,3x($-CH_3$ & $-CH_2-$))

IR Spectrum (KBr Disc.): 2871 (alkyl C-H str.); 1730 (broad absorption; urethane and ketone C=O str.); 1449 (alkyl C-H def.); 853 (p-disubstituted aromatic out-of-plane C-H def.) cm^{-1}

UV Spectrum (DMF): λ_{max} = 289 nm; photoreactive group content = 58%.

6.2.2.3 Advancement of 4,4'-Dihydroxybenzil with Triethyleneglycol Bis(Chloroformate)

Attempting to perform this reaction using the procedure followed to prepare benzil-4,4'-bis(n-butyl carbonate) resulted in decomposition, presumably caused by the presence of water. The aqueous sodium hydroxide used previously was, therefore, replaced by anhydrous potassium carbonate.

Procedure I

To a stirred solution of 2.42g (0.01 mol) 4,4'-dihydroxybenzil and 2.76g (0.02 mol) anhydrous potassium carbonate in tetrahydrofuran were added, dropwise, 3.03g (0.01 mol) triethyleneglycol bis(chloroformate). The reaction mixture was stirred for 48 hrs at room temperature before filtering off the potassium carbonate and evaporating the solvent from the filtrate. Attempting to purify a quantity of the oily product thus formed by Kugel distillation resulted in decomposition. Spectral analysis of the remaining product indicated that the desired material had not been formed.

Procedure II

4.10 ml (0.02 mol) triethyleneglycol bis(chloromformate) were slowly added dropwise to a stirred solution of 4.82g (0.02

mol) 4,4'-dihydroxybenzil and 8.64g (0.04 mol) 25% sodium methoxide in 50ml anhydrous methanol in a flask fitted with a reflux condenser. A solid precipate formed on stirring the solution overnight, and this was isolated by filtration. Drying for several hours in a vacuum oven at 35°C afforded a product yield of 20%.

NMR spectral analysis indicated the presence of some unreacted triethyleneglycol bis(chloroformate), hence the product was placed on a vaccum pump. Unfortunately, this resulted in the solid turning rubbery and failing to show a melting point up to a temperature of 300°C. It was not possible to incorporate the vacuum dried product into a UV-curable composition.

6.2.2.4 Advancement of Benzil-4,4'-Diglycidyl Ether with 5,5-Dimethylhydantoin

The procedure used for the advancement of benzil-4,4'-diglycidyl ether with 5,5-dimethylhydantoin is based upon that used for the similar advancement of the 4,4'-diglycidyl ether of 4,4'-dihydroxy chalcone[25].

Procedure

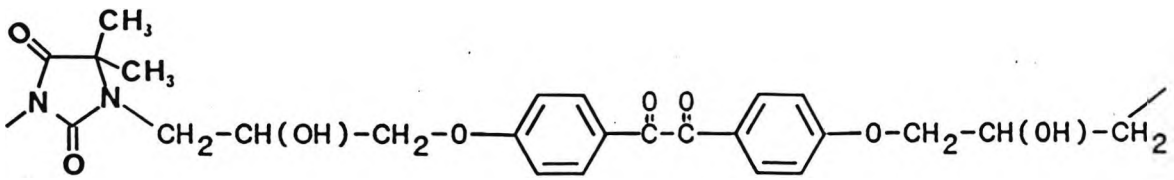
5.03g (0.0142 mol) benzil-4,4'-diglycidyl ether, 1.38g

(0.0108 mol) 5,5-dimethylhydantoin, 1.02 x 10^{-2}g (0.2% by weight) tetramethyl-ammonium chloride and 9.57g 2-ethoxyethanol were combined in a three-necked, round-bottomed flask. The flask was wrapped in aluminium foil to prevent the initiation of crosslinking by UV light. The reaction mixture was then heated to 115°C, stirring continuously. 3ml aliquots of the hot solution were removed at 15-minute intervals and were added to an excess of petroleum ether (60-80°C fraction). The viscous oils thus formed were extracted into chloroform and were isolated by solvent evaporation in vacuo. On storing for several days at room temperature it was observed that, whilst the aliquot removed after 15 minutes retained its bright yellow colour, all of the others began to darken. It was thus concluded that the first sample was the most stable. The above procedure was repeated, therefore, with the entire contents of the reaction vessel being poured into petroleum ether after heating for 15 minutes. After evaporation of the chloroform in vacuo, the sample was placed on a vacuum pump to remove any remaining traces of solvent.

NMR Spectrum ($CDCl_3$): δ 8.30-8.12 (d,4H,J=9Hz;benzoyl); 7.60-7.04 (d,4H,J=9Hz; aryl); 4.52-4.11 (m,4H,2x-CH_2-OAr); 2.65-2.33 (m,4H,-CH_2-N); 2.01-1.80 (m,2H,-CH-OH); 1.14 (s,6H,2x-CH_3)

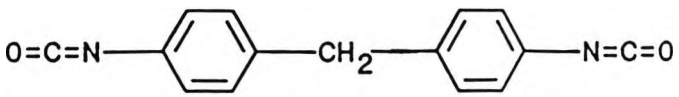
IR Spectrum (NaCl windows): 3413 (O-H str.); 2932 (alkyl C-H str.); 1768 & 1710 (hydantoin C=O str.'s); 1668 (benzil C=O str.); 1598, 1571 & 1507 (aryl C-C str.); 1447 (alkyl C-C str.); 1423 & 1375 ($-CH_3$ C-H bend); 1264 & 1064 (alkyl aryl ether C-O str.); 845 (p-disubstituted aromatic out-of-plane C-H def.) cm^{-1}

UV Spectrum(Chloroform) λ_{max} = 302 nm; photoreactive group content = 56%



Copolymer of Benzil-4,4'-Diglycidyl Ether & 5,5-Dimethylhydantoin

6.2.2.5 Advancement of 4,4'-Diaminobenzil with Methylene Diphenyl Diisocyanate

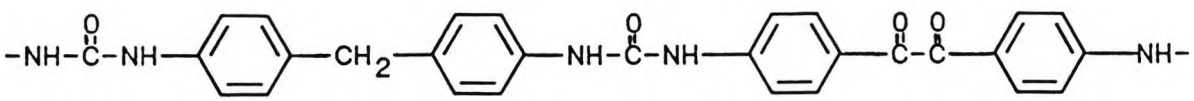


Methylene Diphenyl Diisocyanate, MDI

Procedure

2.40g (0.01 mol) 4,4'-diaminobenzil were added to a stirred solution of 2.50g (0.01 mol) MDI in 250ml N,N-dimethylformamide. T.L.C. analysis (CH_2Cl_2/MeOH 95:5) showed all the starting material to have been consumed after stirring the reaction mixture for 1 hour at room temperature. Adding ethanol to the N,N-dimethylformamide solution resulted in the precipitation of a pale yellow solid, which was isolated by filtration through a No. 4 glass sinter.

The product, which was dried overnight in a vacuum oven at 40°C, was obtained in 53% yield. All attempts to dissolve the poly(disubstituted urea) in common laboratory solvents were unsuccessful. Consequently, it was decided to replace MDI with an aliphatic diisocyanate, in the hope that this would lead to a polymeric product with better solubility in the available solvents.



Poly(disubstituted urea) formed by the reaction of 4,4'-diaminobenzil with MDI

6.2.2.6 Advancement of 4,4'-Diaminobenzil with 1,6-Diisocyanatohexane

Procedure

0.80g (3.30×10^{-3} mol) 4,4'-Diaminobenzil was added to a stirred solution of 0.50g (3.00×10^{-3} mol) 1,6-diisocyanatohexane in 2.5ml N,N-dimethylformamide. The solution was stirred at room temperature for 1 hour before adding an excess of ethanol and refrigerating overnight. A very small quantity of product was isolated, yield = 12%. Whilst being slightly soluble in dimethyl sulphoxide, the product was found to be insoluble in all other common laboratory solvents.

NMR Spectrum (DMSO-d_6): δ 9.05 (s,2H,2x-NH-); 7.87-7.43 (m,4H,benzoyl);6.71-6.20 (m,4H,aryl);3.40-2.77 (m,4H,2x-CH_2N) 1.63-0.98 (m,8H,4x -C-CH_2-C-);

IR Spectrum (KBr Disc.): 3359 (N-H str.); 2935 & 2860 (alkyl C-H str.); 1660 (broad absorption; urea & ketone C=O str .); 1589 (aryl C-C str.), 1535 (urethane C-O str./N-H def.); 847 (p-disubstituted aromatic out-of-plane C-H def.) cm^{-1}

6.2.2.7 Advancement of 4,4'-Diaminobenzil with Isophorone Diisocyanate

It was attempted to advance 4,4'-diaminobenzil with isophorone diisocyanate, using a similar procedure to that described on p. 312. However, no reaction took place, even when stirring for several days at an elevated temperature.

6.2.2.8 Advancement of 4,4'-Diaminobenzil with Triethyleneglycol Bis(Chloroformate)

Procedure

1.20g (0.005 mol) 4,4'-Diaminobenzil were dissolved in 15ml tetrahydrofuran. To this was added a solution of 0.40g (0.100 mol) sodium hydroxide in 1.5ml water. 1.00ml (0.005 mol) triethyleneglycol bis(chloroformate) was added dropwise, down a reflux condenser, to the stirred diaminobenzil mixture. The reaction mixture was stirred at room temperature overnight, after which time T.L.C. analysis (CH_2Cl_2/MeOH 5:1) showed that no starting material remained. The organic and aqueous layers were then separated and the organic layer was dried over anhydrous sodium sulphate. Solvent evaporation yielded a yellow gum, which became unmanageable upon attempted extraction into chloroform. The product was, therefore, not isolated.

6.2.2.9 Advancement of 4,4'-Dihydroxybenzoin with Isophorone Diisocyanate

Procedure

4.88g (0.02 mol) 4,4'-dihydroxybenzoin were dissolved in 10ml N,N-dimethylformamide and added to a solution of 4.00g (0.02 mol) isophorone diisocyanate and 0.19g (2.02×10^{-3} mol) phenol in 20ml N,N-dimethylformamide. After stirring the mixture at room temperatures for several hours, T.L.C. analysis (CH_2Cl_2/MeOH 95:5) showed the reaction to have reached completion. Adding ethanol to the N,N-dimethylformamide failed to effect precipitation of the product. The ethanol was, therefore, removed *in vacuo* and the reaction mixture was poured into water. The aqueous solution was extracted three times with ether, which resulted in the formation of a pale yellow solid. This solid was dissolved in acetone and the acetone solution was dried over anhydrous potassium carbonate. Solvent evaporation afforded a viscous yellow oil, the NMR spectrum of which showed a very large amount of N,N-dimethylformamide to be present.

Attempting to dry the product on a vacuum pump resulted in it forming a gum which stuck to the sides of the flask and could not be dissolved in any of the common laboratory solvents. Consequently, this product, also, was not isolated.

6.2.3 DETERMINATION OF PHOTOREACTIVE GROUP CONTENTS OF POLYMERIC PHOTOINITIATORS

The photoreactive group contents of the various polymeric photoinitiators were detemined by UV spectroscopy, comparing the molar absorptivities to those of the corresponding benzil or benzoin monomers.

The Beer-Lambert law can be expressed as $\varepsilon = A/_{cl}$[26], where ε is the molar absorptivity, A is the absorbance of the solution, c is the solute concentration (in mol dm^{-3}) and l is the path length of the sample (in cm). It was assumed that the molar absorptivity of a solution of a given polymeric photoinitiator was directly proportional to the concentration of chromophoric groups in the polymer. Thus, if ε were known for the corresponding benzil or benzoin monomer, the concentration in the given polymeric photoinitiator could be evaluated by application of the Beer-Lambert law to solutions of the polymer of known concentration.

Thus, UV spectra were recorded for each of the isolated polymeric photoinitiators and their corresponding monomeric photoinitiators.

6.2.4 SCREENING OF POLYMERIC PHOTOINITIATORS

Solutions of the polymeric photoinitiators in tetra-ethyleneglycol diacrylate (T.E.G.D.A.) were prepared such that the concentration of photoreactive groups was 0.1M. Another set of similar solutions was prepared, but these also had a 0.6M concentration of N-methyldiethanolamine. Films of 6μm thickness of the solution were coated onto strips of G.N.T. paper and cured on a Colordry UV curing apparatus. The same solutions were also used for real-time infra-red spectroscopic analysis, but with a film thickness of 24μm on acetate strips.

6.3 RESULTS & DISCUSSIONS

Due to problems encountered in isolating and dissolving the polymeric photoinitiators, UV spectra and UV curing data were obtained for only three samples.

6.3.1 PHOTOREACTIVE GROUP CONTENTS OF POLYMERIC PHOTOINITIATORS

The solvent used for each polymeric photoinitiator was the same as that used for the corresponding parent monomer.

The following abbreviations are used to denote the polymeric photoinitiators:

Comonomers from which Polymers Derived	Polymer Abbreviation
4,4'-Dihydroxybenzil/1,6-Diisocyanato-hexane	HDI
4,4'-Dihydroxybenzil/Isophorone Diisocyanate	HIS
Benzil-4,4'-Diglycidyl Ether/ 5,5-Dimethylhydantoin	GLYC

The solvents in which the UV spectra of the polymeric photoinitiators and their corresponding parent monomers were recorded are as follows:

Polymeric Photoinitiator	Parent Monomer	Solvent
HDI	4,4'-Dihydroxybenzil	DMF
HIS	4,4'-Dihydroxybenzil	DMF
GLYC	Benzil-4,4'-Diglycidyl Ether	$CHCl_3$

On the basis that 1:1 alternating copolymers would be produced, the theoretical photoreactive group content, by weight, was calculated for each of the polymeric photoinitiators. These values were then compared to those found experimentally by UV spectral analysis.

	Photoreactive Group Content by Weight (%)	
Photoinitiator	Theoretical	Experimental
HDI	41	85
HIS	52	58
GLYC	48	56

It can be seen that, in each case the incorporation of the benzil-derived monomer is higher than would be expected. Whilst the difference is hardly significant for the polymeric photoinitiators HIS and GLYC, the polyurethane HDI was found to have a photoreactive group content of more than twice the theoretically predicted value. There seems to be no obvious reason for this observation.

6.3.2 SCREENING OF POLYMERIC PHOTOINITIATORS

In each case, the polymeric photoinitiators were compared with their parent benzil monomers. In this way the effect of incorporation of the photoreactive groups into a polymeric backbone could be observed.

The monomeric and polymeric photoinitiators are denoted by codenames as follows:

Photoinitiator	Codename
4,4'-Dihydroxybenzil	DHB
4,4'-Dihydroxybenzil/1,6-Diisocyanatohexane Urethane	HDI
4,4'-Dihydroxybenzil/Isophorone Diisocyanate Urethane	HIS
Benzil-4,4'-Diglycidyl Ether	BDG
Copolymer of Benzil-4,4'-Diglycidyl Ether with 5,5-Dimethylhydantoin	GLYC

In order to obtain solutions of the photoinitiators in tetraethyleneglycol diacrylate, it was first necessary to dissolve them in a small quantity of organic solvent. The solvents used in each case are recorded,as follows:

Photoinitiator	Solvent
DHB	Dichloromethane
HDI	Dimethylsulphoxide
HIS	Acetone
BDG	Chloroform
GLYC	Acetone

6.3.2.1 UV Curing Measurements

Tetraethyleneglycol diacrylate (T.E.G.D.A.) films of 6 μm thickness were cured on a G.N.T. paper substrate.

Curing in the Absence of a Tertiary Amine Synergist

Photo-initiator	No. of Passes Required to Cure Film at Specified Belt Speed (m min^{-1})									
	14	16	20	21	30	36	43	51	58	72
DHB	17	19	26	-	-	-	-	-	-	-
HDI	19	21	28	-	-	-	-	-	-	-
HIS	20	22	26	-	-	-	-	-	-	-
BDG	12	12	16	20	26	-	-	-	-	-
GLYC	14	14	16	19	20	24	29	-	-	-

Curing in the Presence of N,-Methyldiethanolamine

Photo-initiator	No. of Passes Required to Cure Film at Specified Belt Speed (m min^{-1})									
	14	16	20	21	30	36	43	51	58	72
DHB	3	4	4	5	7	8	10	13	16	21
HDI	4	4	4	5	5	8	8	8	11	14
HIS	3	3	3	4	5	6	7	8	11	13
BDG	1	1	1	1	1	2	2	2	2	2
GLYC	1	1	1	1	1	1	2	2	3	3

As expected, the performance of each photoinitiator was enhanced significantly by the addition of N-methyldiethanolamine.

The polyurethanes HDI and HIS actually appeared to be slightly less efficient in the absence of amine, than the dihydroxybenzil from which they were derived. However, curing was only achieved with a very few, slow belt speeds, and the number of passes required with each of the three photoinitiators was very similar. There is, therefore, very little which can be said about the effect of incorporation of the monomeric photoinitiators into a polymeric backbone, based upon the curing measurements in the absence of amine. The

results obtained in the presence of N-methyldiethanolamine, however, were rather more informative. Whereas there was little difference between the rates of cure obtained at low belt speeds, the polyurethane clearly initiated the photo-polymerization of T.E.G.D.A. with greater efficiency than the dihydroxy monomer at the higher belt speeds.

Considering, now, the diglycidyl ether (BDG) and its copolymer (GLYC), in this case a difference in efficiencies could be seen in the absence of amine. Under these conditions, cure could be effected with the polymeric photoinitiator up to a belt speed of 43m min^{-1}. With the monomeric diglycidyl ether, on the other hand, cure was not effected above a belt speed of 30m min^{-1}. Both of these photoinitiators afforded very high rates of cure in the presence of N-methyldiethanolamine, and little difference in their photoinitiating efficiencies was observed under these conditions.

Thus, the UV curing results seem to indicate that the efficiency of the monomeric Type II photoinitiators is enhanced by incorporation into the backbone of a polymer chain.

Aromatic ketones such as benzil produce initiating radicals by intermolecular hydrogen abstraction from a hydrogen donor[27].

$$^{3}PI + R—H \longrightarrow PIH^{\cdot} + R^{\cdot}$$

PI = photoinitiator

R-H = hydrogen donor

The hydrogen abstraction process produces two radicals which are both potential initiators of free radical polymerization. Both indirect[28,29] and direct[30,31] evidence has been furnished in support of the hydrogen donor-derived radicals being the ones which are active in initiation. With benzophenone as photoinitiator and tetrahydrofuran as the hydrogen donor, it was shown that the donor-derived radical was a far more effective initiator than the benzophenone ketyl radical. The latter was found to function primarily as a chain-terminating agent[32].

The UV curing results presented in this chapter indicate that the polymer-bound benzil-type photoinitiators are more efficient than their free, monomeric counterparts. With N-methyldiethanolamine as coinitiator, it is the amine-derived radical which is active in initiation and not the benzil ketyl radical - whether bound or free.

Thus, the observed efficiency trends cannot be explained in terms of protection of the propagating radicals by the polymer coils, since the propagating radicals were not polymer-bound. One possible explanation is the operation of a Trommsdorff-type effect.

With the polymeric photoinitiators, the total concentration of polymeric material in the polymerization medium would very quickly reach high levels. A corresponding viscosity increase would result, restricting the movement of the radicals. Being monomeric and relatively small in size, the amine-derived propagating radicals would be far less affected by these viscosity effects than the polymer-bound ketyl radicals. Thus, whilst polymerization was able to proceed, the high viscosity of the polymerization medium would result in termination becoming increasingly slower. With monomeric photoinitiators, the formation of such high concentrations of polymeric material would be slower and, furthermore, both types of radicals would be free and less affected by high viscosities. It was to be expected, therefore, that the polymer-bound photoinitiators would afford higher rates of polymerization than their unbound counterparts.

Another possible explanation for the higher polymerization rates afforded by the polymeric photoinitiators is that energy migration occurred along the polymer backbone.

6.3.2.2 Monitoring Relative Rates of Cure by Real-Time Infra-red Spectroscopic Analysis

Measurements in the Absence of N-Methyldiethanolamine

Photo-initiator	Relative Polymerization Rate After Exposure to UV for t secs t = 0	3	6	30	Induction Period (secs)
DHB	0.00	0.09	0.08	0.05	0.60
HDI	0.00	0.06	0.06	0.01	1.74
HIS	0.42	0.98	0.68	0.12	0.00
BDG	2.73	0.84	0.67	0.16	0.00
GLYC	1.39	0.88	0.63	0.06	0.00

Measurements in the Presence of N-Methyldiethanolamine

Photo-initiator	Relative Polymerization Rate After Exposure to UV for t secs t = 0	3	6	30	Induction Period (secs)
DHB	3.31	0.76	0.30	0.04	0.00
HDI	0.89	0.19	0.21	0.05	0.00
HIS	2.73	0.74	0.38	0.04	0.00
BDG	5.00	0.97	0.76	0.03	0.00
GLYC	3.90	0.41	0.14	0.02	0.00

In the absence of amine, very low polymerization rates were obtained with DHB and the two polyurethanes derived from it. In fact, induction periods were obtained with DHB and HDI. Relatively little change in polymerization rates was observed with these three initiators throughout the irradiation period.

The addition of a tertiary amine produced a marked improvement in the performance of the photoinitiators, with the highest rates of polymerization being achieved at t=0. The maximum cure rate with HDI was still found to be relatively low, however. The diol DHB also gave faster initial rates of cure than the other polyurethane, HIS. Cure rates at t=30 were virtually the same for all three photoinitiators in the presence of N-methyldiethanolamine.

Considering the photoinitiators BDG and GLYC, it can be seen that both of these afforded fairly high cure rates even in the absence of a tertiary amine. (As discussed in Chapter 5 [see p. 278], the observation of photopolymerization with the Type II photoinitiators in the absence of a hydrogen donor is most probably attributable to minute traces of water in the reagents.)

The addition of N-methyldiethanolamine resulted in even higher rates at t=0 and lower rates at t=30, indicating that the curing process started and reached completion more rapidly under these conditions. Both in the absence and presence of amine, higher initial rates were obtained with the monomer than with the polymeric photoinitiators.

The results obtain from RTIR spectroscopic analysis show that, for the photoinitiators under consideration, incorporation of the monomers into a polymeric backbone led to a decrease in the initial rate of cure. It is possible that this was a direct result of the size of the polymeric photoinitiators. The polymer coils would be expected to hinder the approach of the tertiary amine to the ketone moieties and thus hinder the production of initiating radicals. Once the initiating radicals had been formed, polymerization could proceed rapidly, with the bulkiness of the polymer-bound ketyl radicals reducing their efficiency in the termination process. Thus higher rates of polymerization would be expected with the polymeric photoinitiators once the initial retardation had been overcome. Whilst this was not clearly visible from the RTIR measurements, the UV curing results were in agreement with such an effect.

6.4 SUMMARY

Polymeric photoinitiators were prepared in which Type II monomeric photoinitiators were built into the backbone of a polymer chain. RTIR spectroscopic measurements indicated that incorporation of the photoreactive moieties into a polymer backbone led to a decrease in the instantaneous rate of cure upon UV irradiation. Little effect on the overall polymerization rates was observed.

Thin film curing measurements, however, indicated that the overall efficiencies afforded by the polymeric photoinitiators were equal to, if not greater than, those of their parent monomers.

Whilst the results obtained are not conclusive, there would appear to be a strong case for photoinitiators in which the photoreactive moieties are built into a polymeric backbone. In addition to the possibility of enhanced photoreactivity, this would also afford the advantages of reduced migration of photodegradation products, as discussed in previous chapters (see Introduction to Polymeric Photoinitiators, p. 100)

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APPENDIX I:

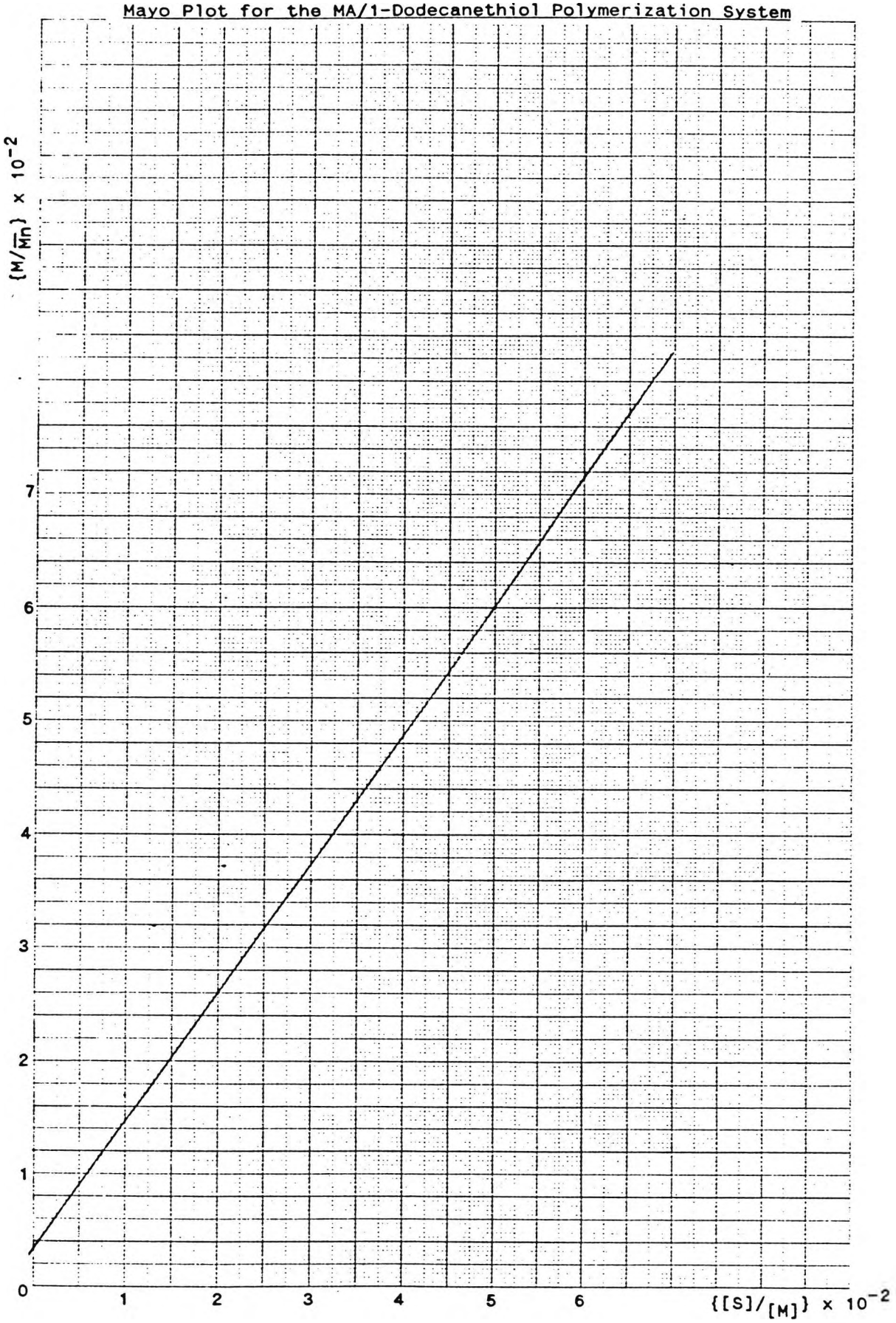
SUPPLEMENTARY DATA

TO

CHAPTER III

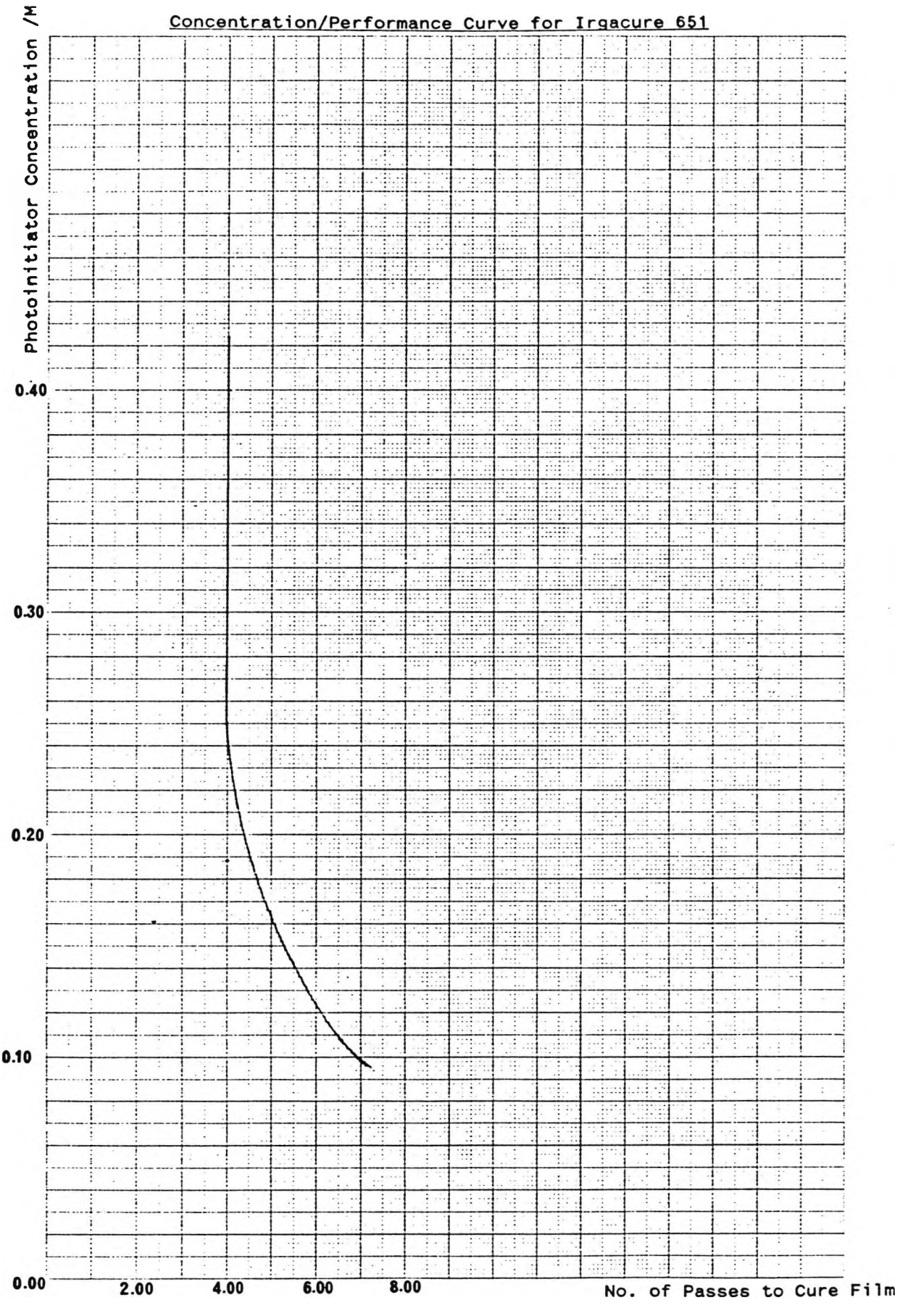
MAYO PLOT

Mayo Plot for the MA/1-Dodecanethiol Polymerization System



CONCENTRATION/PERFORMANCE

CURVES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Photoinitiator Concentration /M
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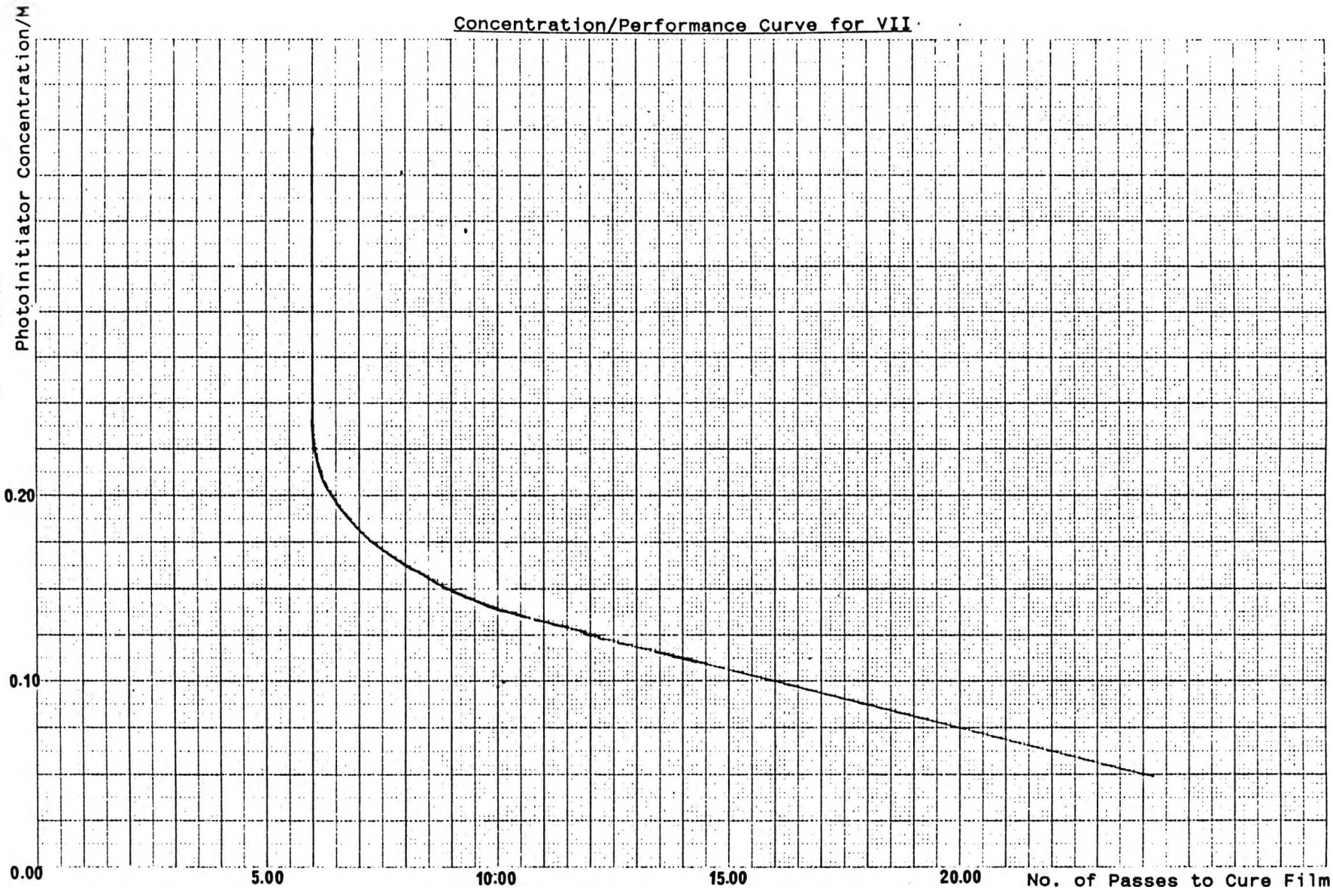
4.00
6.00
8.00
No. of Passes to Cure Film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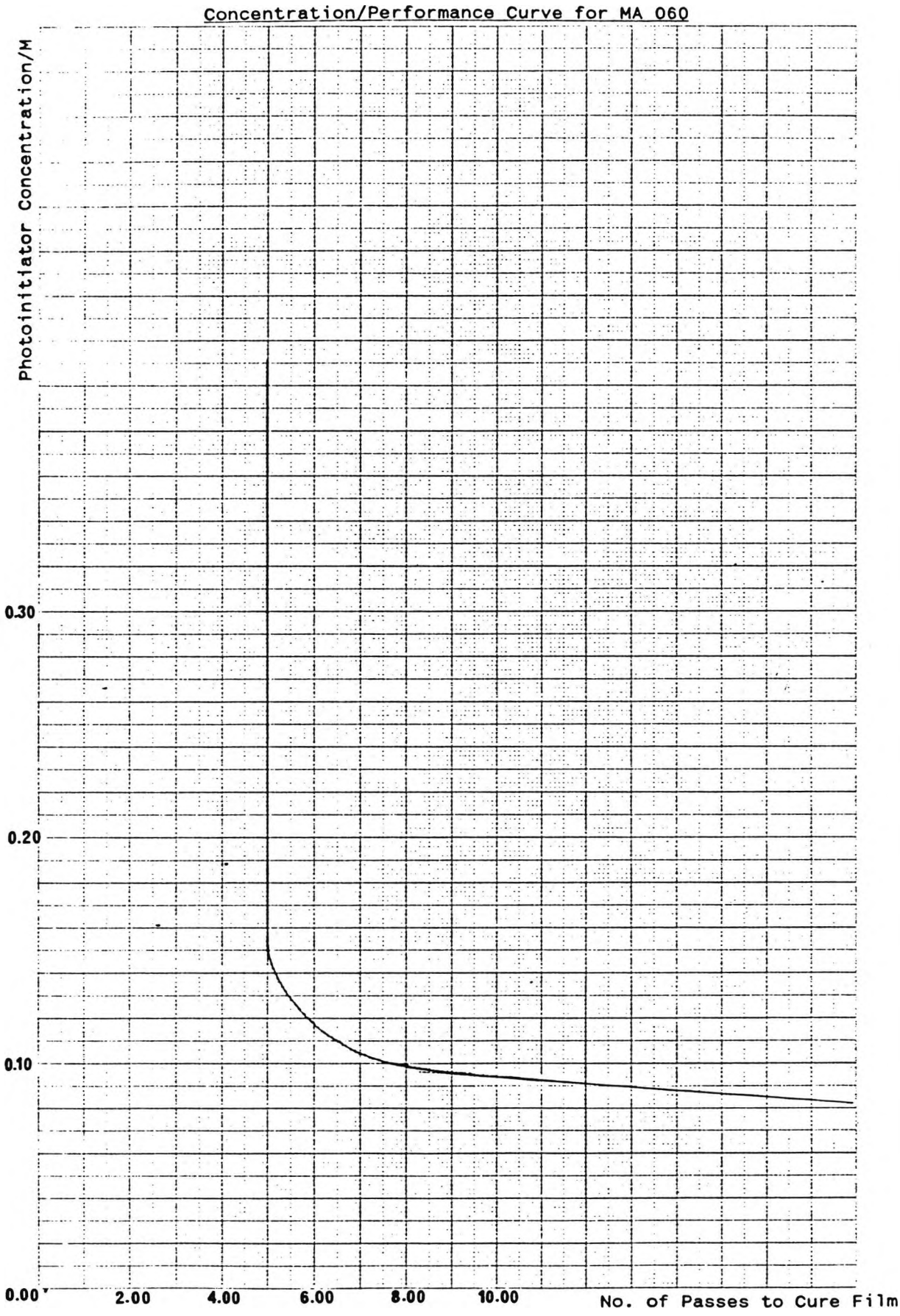
No. of Passes to Cure Film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Photoinitiator Concentration/M
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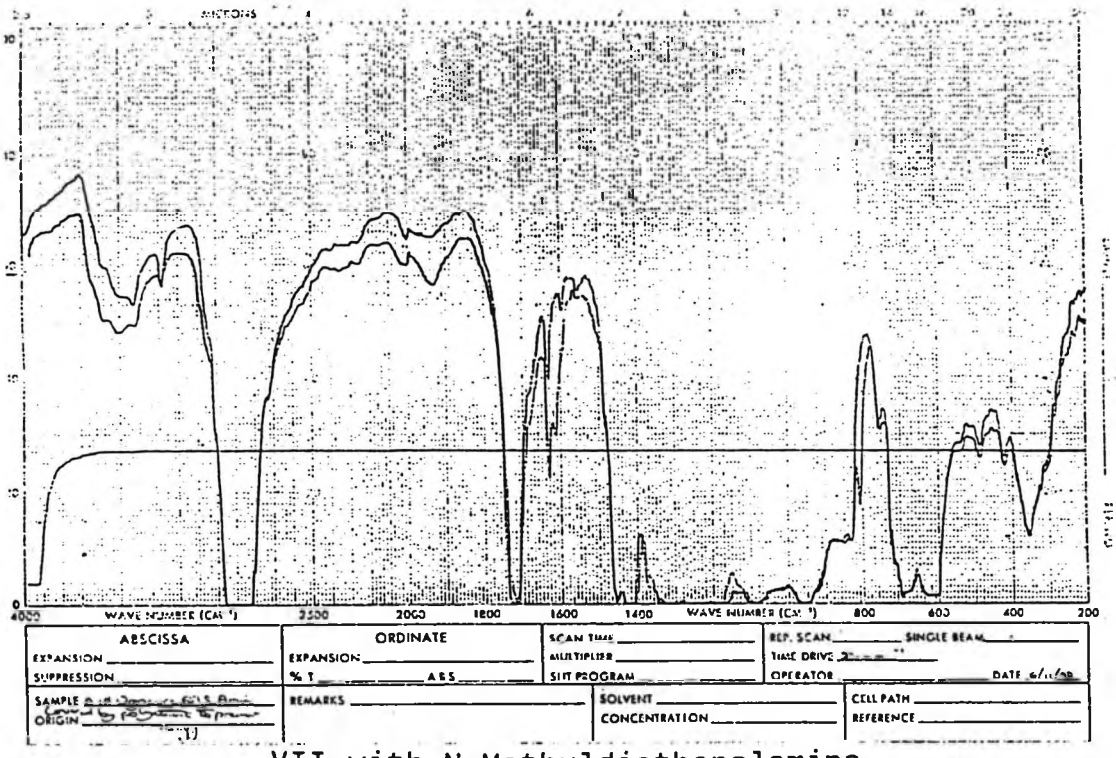
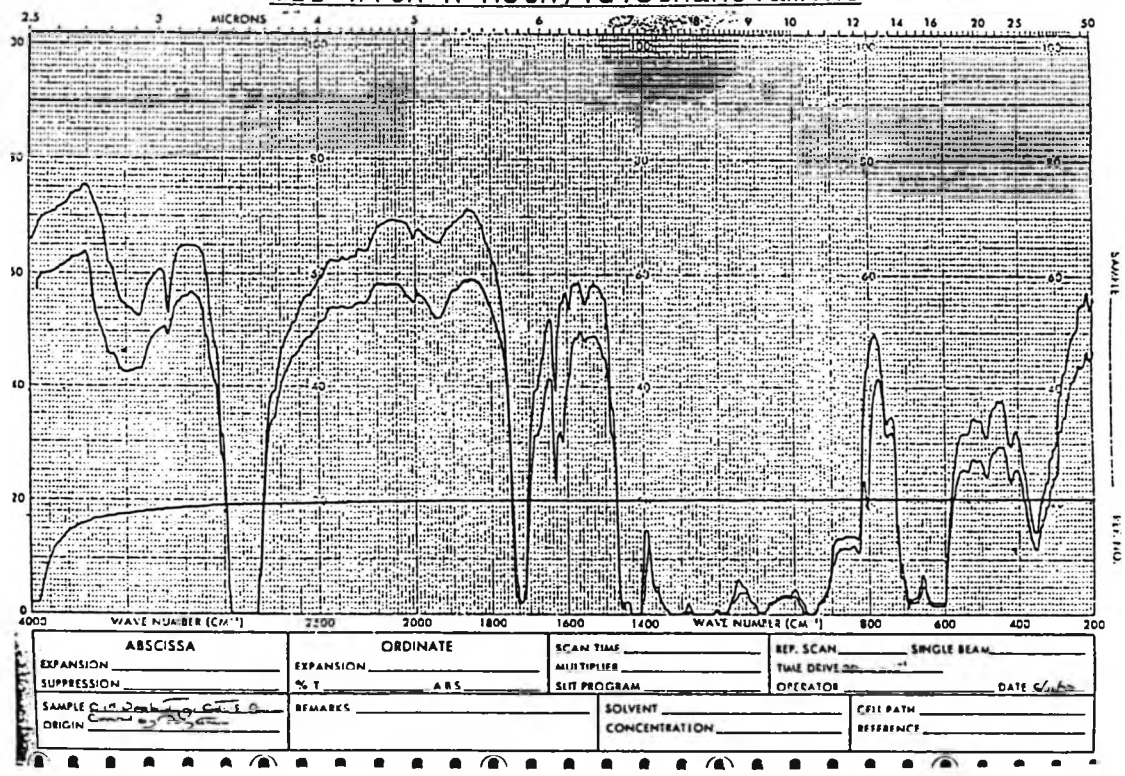
No. of Passes to Cure Film

RTIR SPECTRA

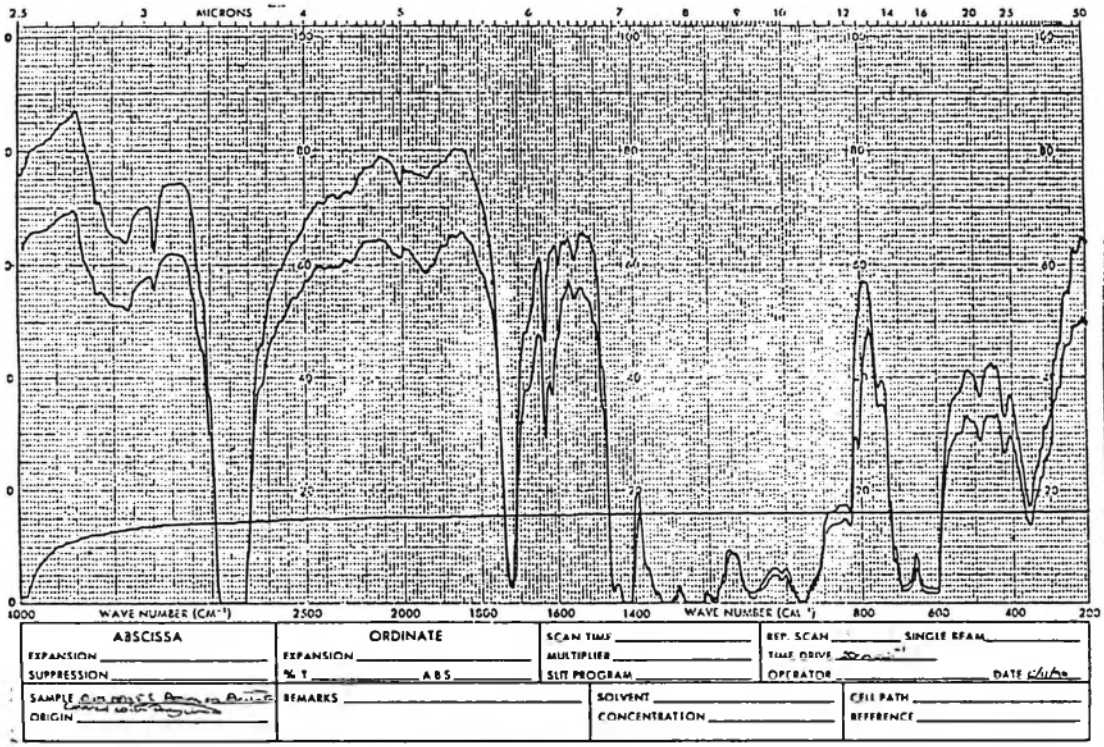
Irgacure 651 with N-Methyldiethanolamine



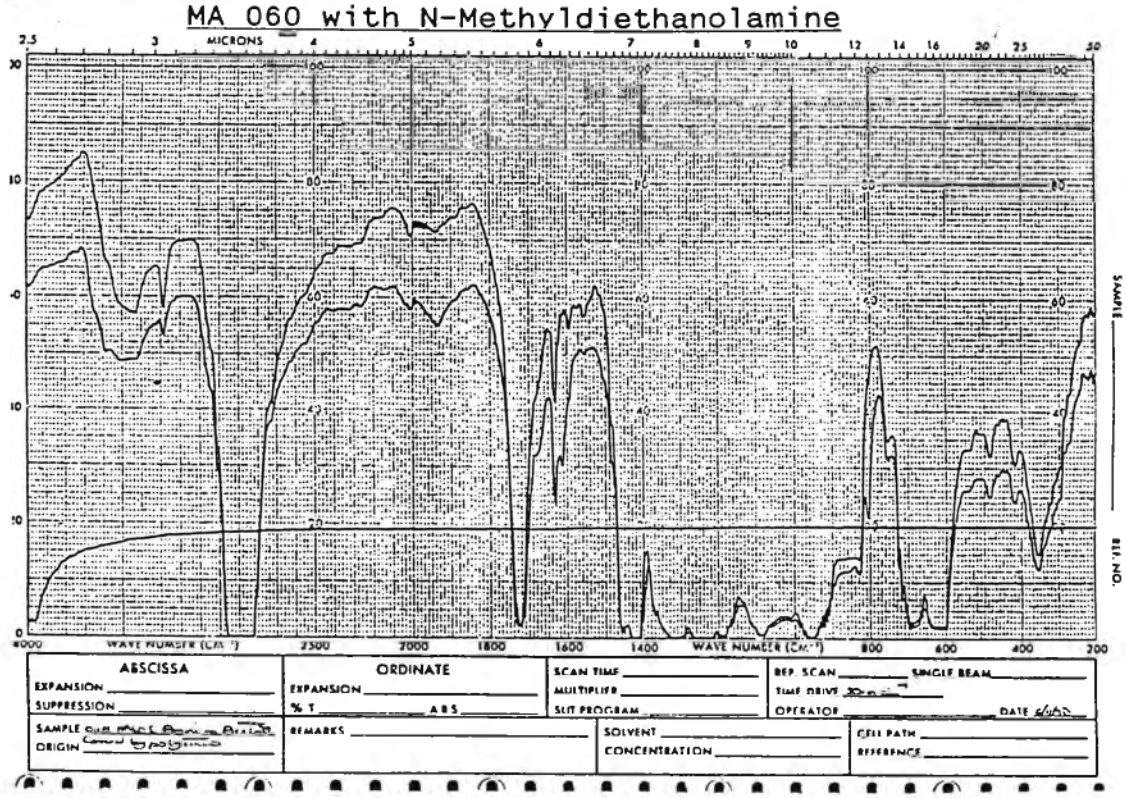
VII with N-Methyldiethanolamine



MA P45 with N-Methyldiethanolamine



MA 060 with N-Methyldiethanolamine



APPENDIX II:

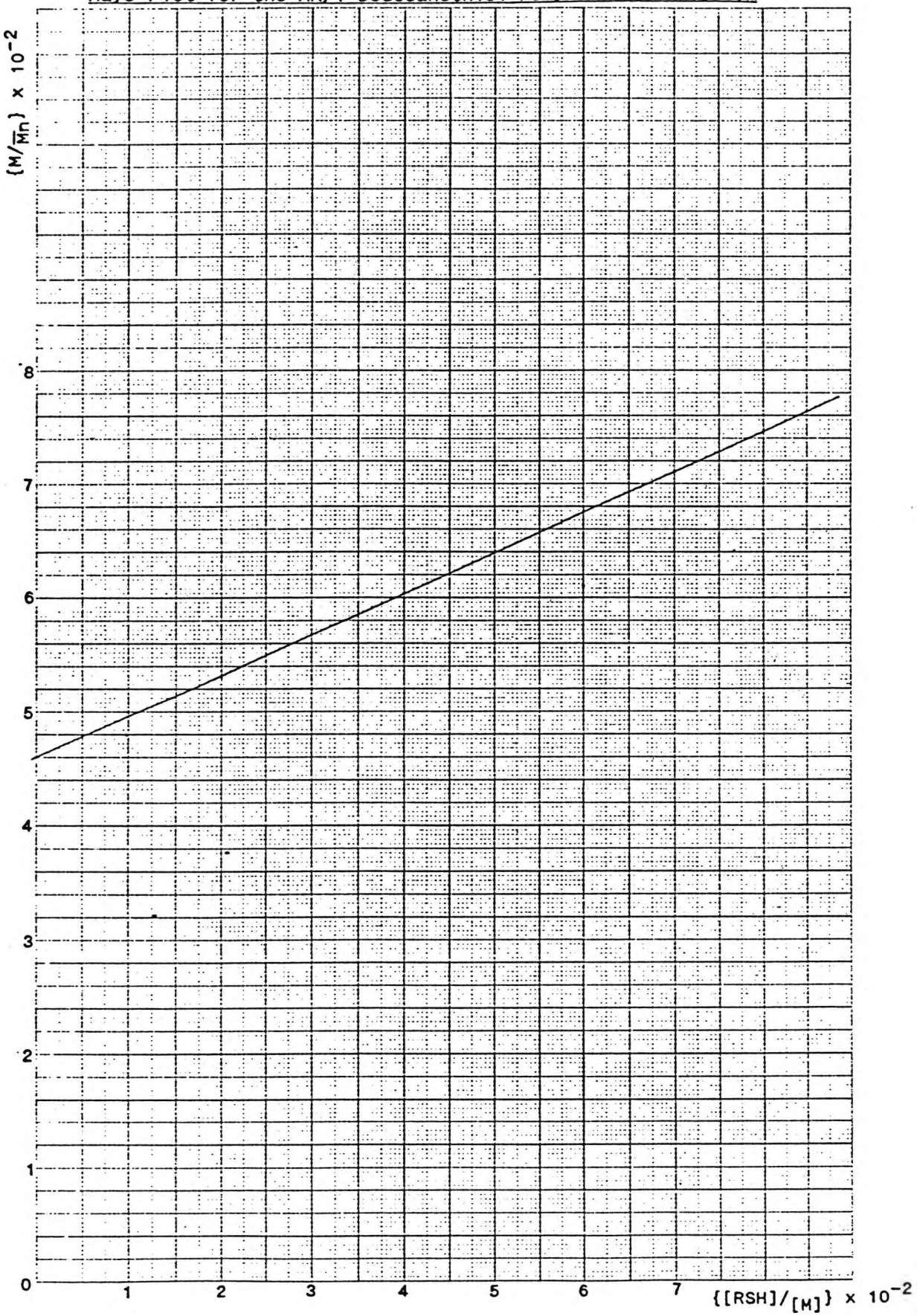
SUPPLEMENTARY DATA

TO

CHAPTER IV

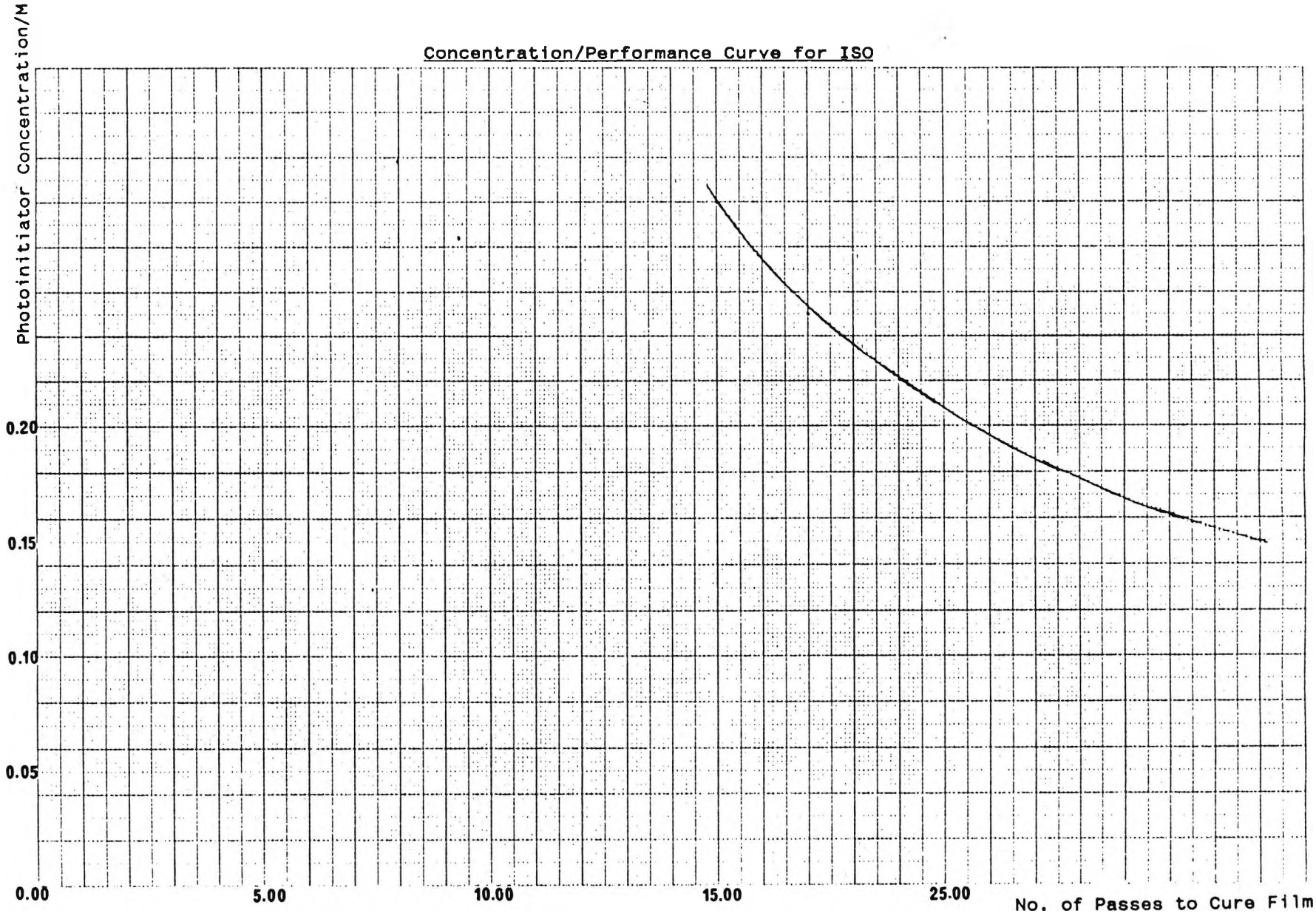
MAYO PLOT

Mayo Plot for the AA/1-Dodecanethiol Polymerization System



CONCENTRATION/PERFORMANCE

CURVES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Photoinitiator Concentration/M
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5.00
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25.00
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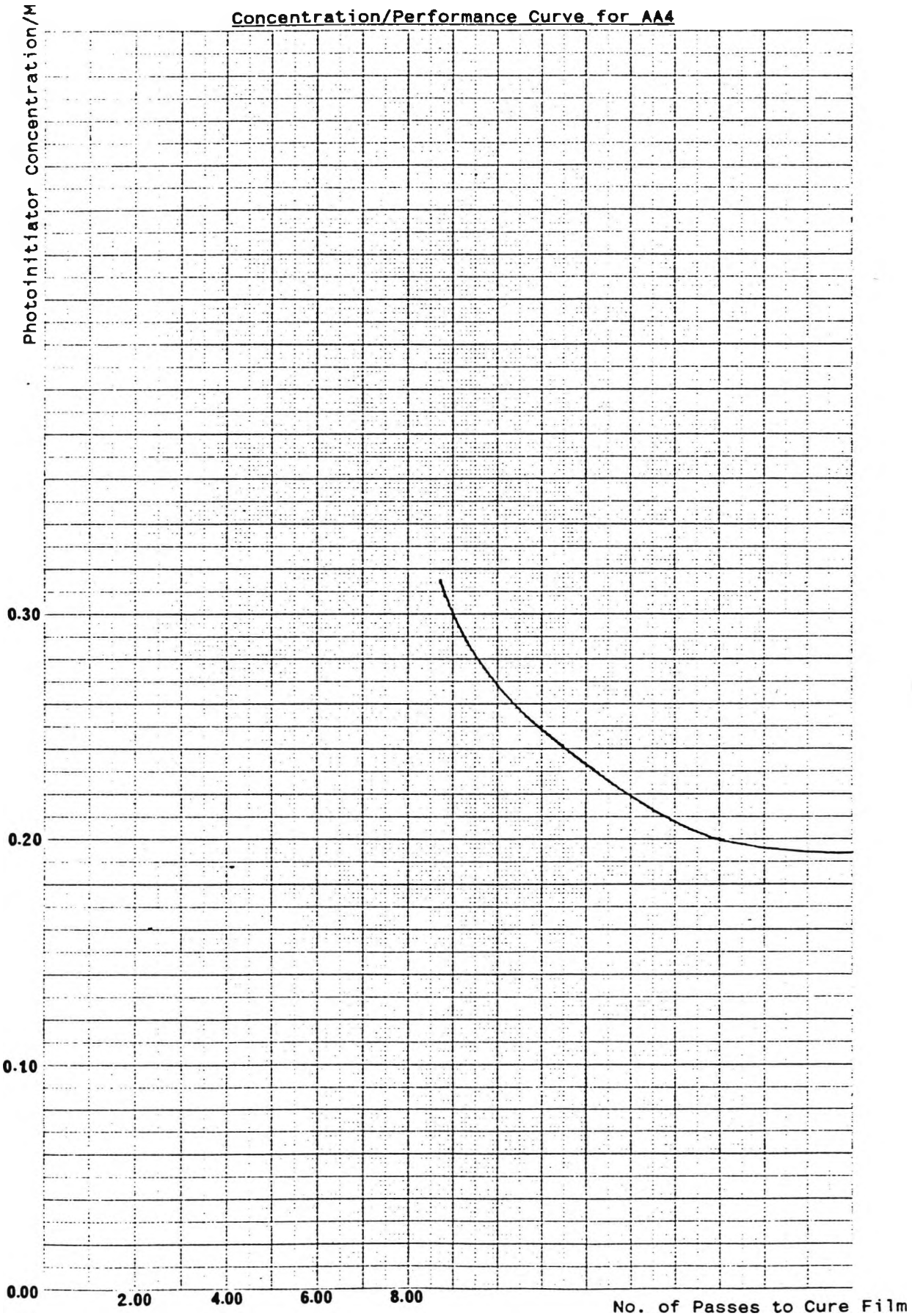
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Photoinitiator Concentration/M
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0.10
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2.00
4.00
6.00
8.00
No. of Passes to Cure Film

APPENDIX III:

SUPPLEMENTARY DATA

TO

CHAPTER V

CONCENTRATION/PERFORMANCE

CURVES

Key to Symbols

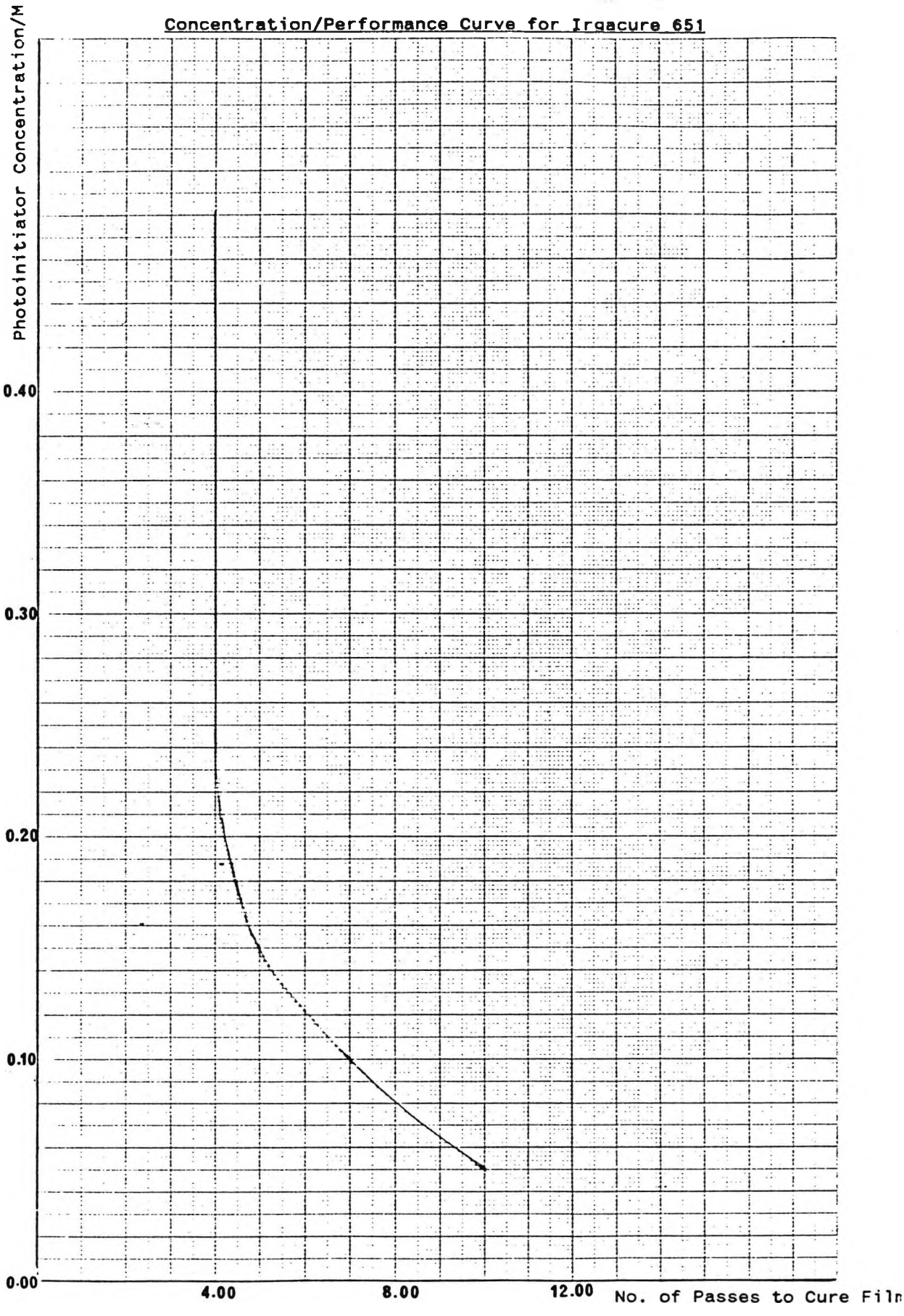
Concentration/Performance Curves

Numeral	Photoinitiator
V	Benzil-4,4'-Diallyloxy Ether
VII	Benzil-4,4'-Diglycidyl Ether
IX	4,4'-Diacetamidobenzil
XI	Benzil-4,4'-Bis(n-Butyl Urethane)
XIII	4,4'-Dihydroxybenzoin
XIX	4,4'-Diacetamidobenzoin

RTIR Spectra

A - Spectra recorded in the absence of N-methyldiethanolamine

B - Spectra recorded in the presence of N-methyldiethanolamine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Photoinitiator Concentration/M
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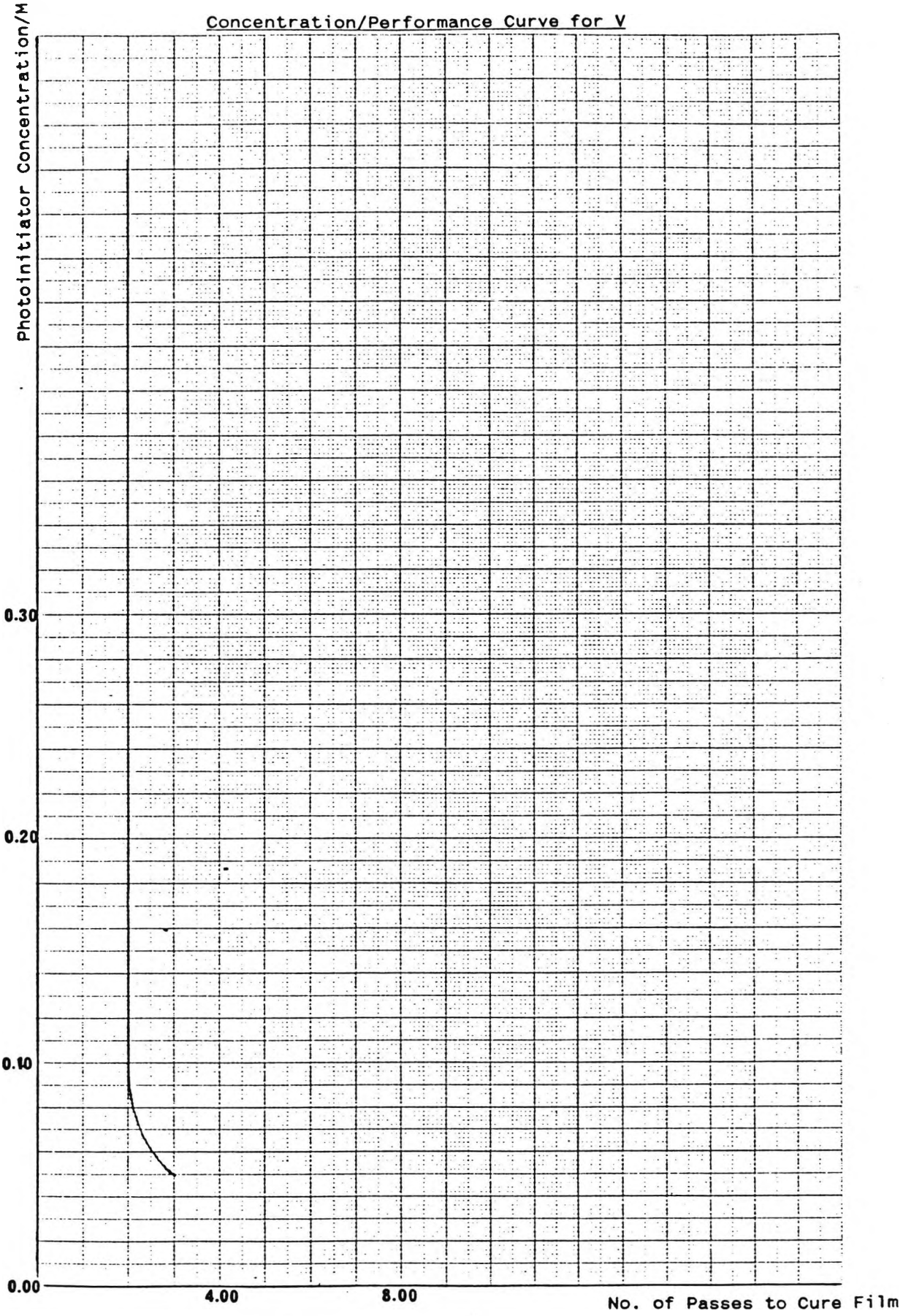
12.00
No. of Passes to Cure Film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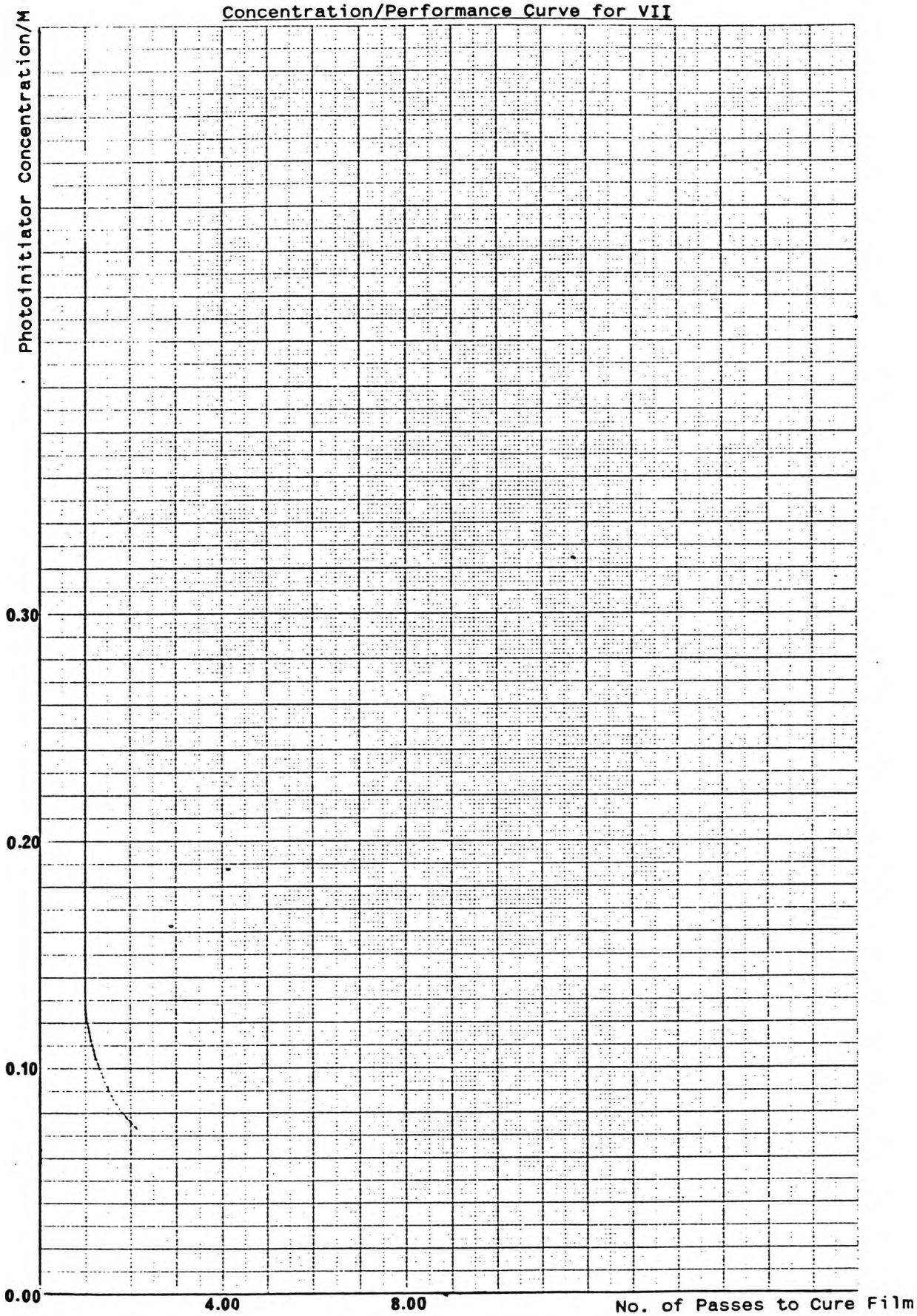
No. of Passes to Cure Film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Photoinitiator Concentration/M
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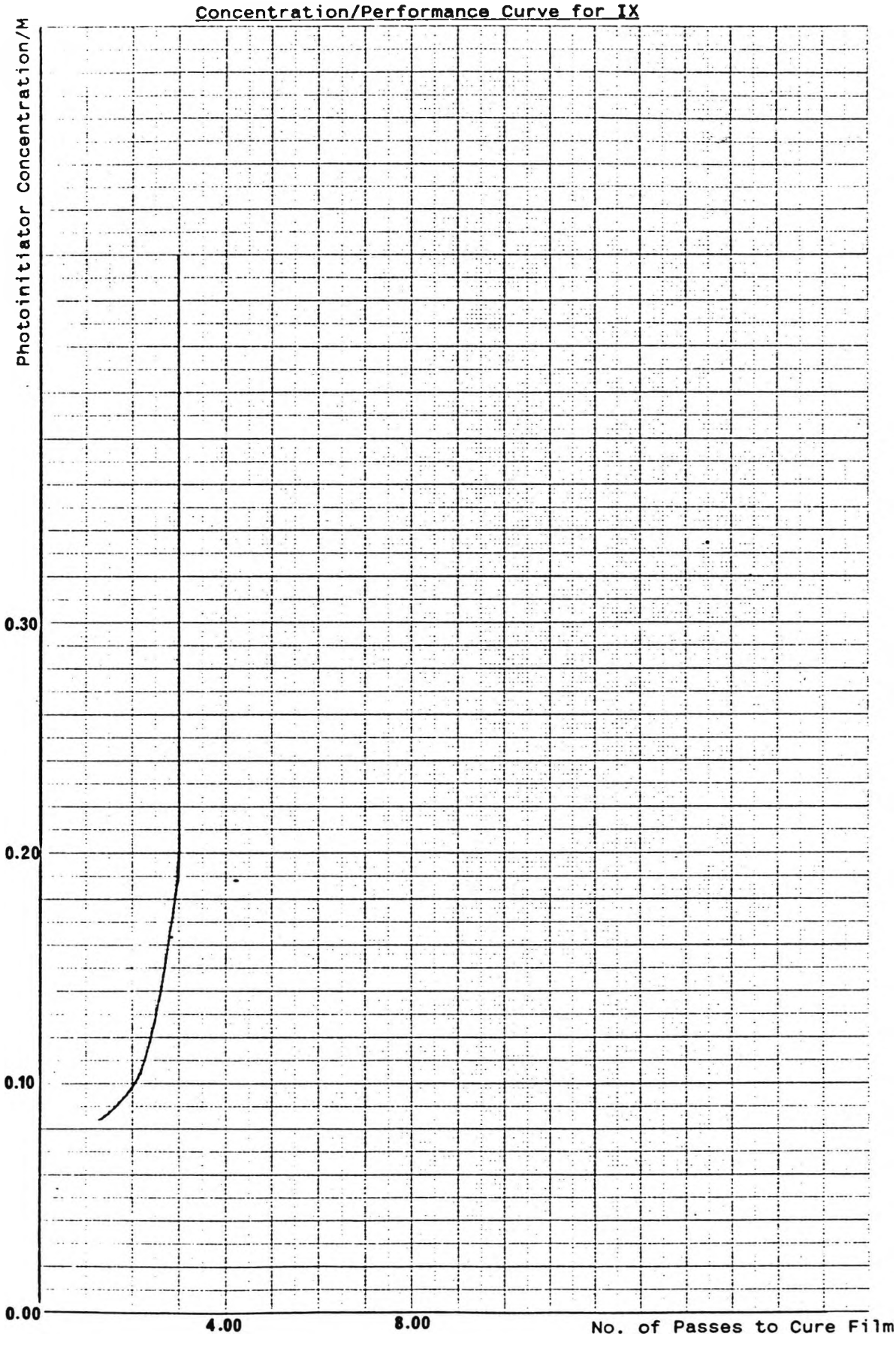
No. of Passes to Cure Film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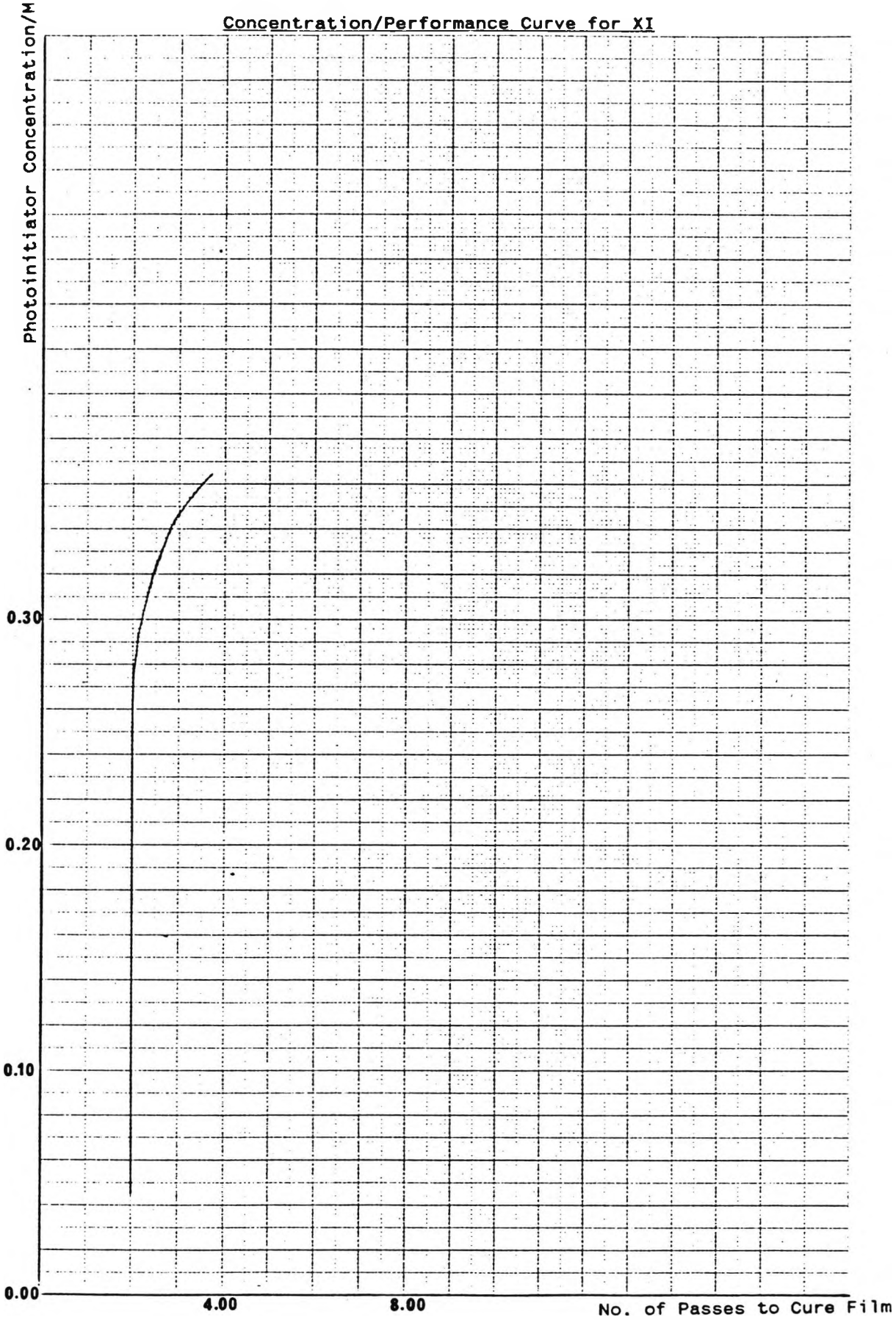
No. of Passes to Cure Film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Photoinitiator Concentration/M
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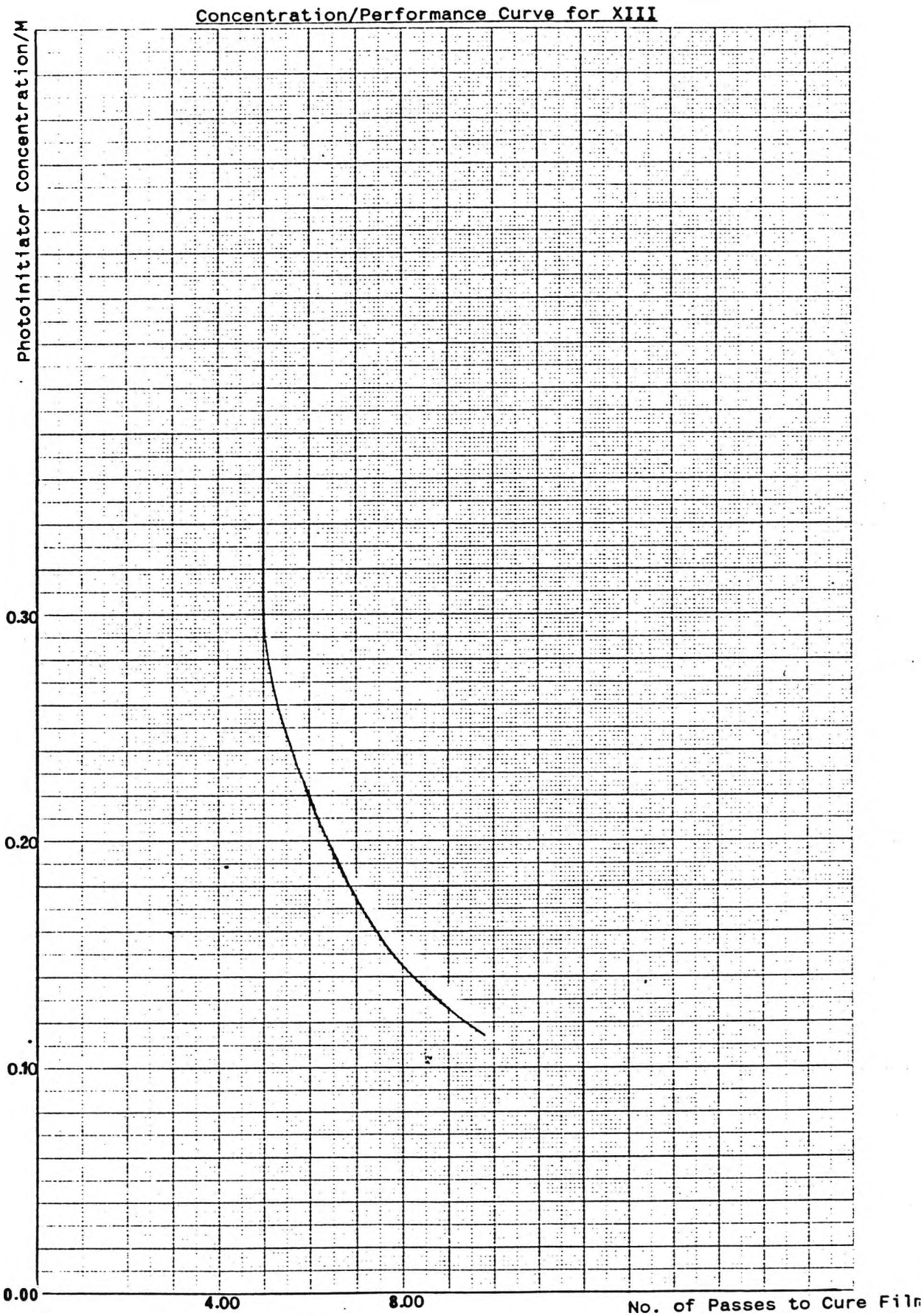
No. of Passes to Cure Film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Photoinitiator Concentration/M
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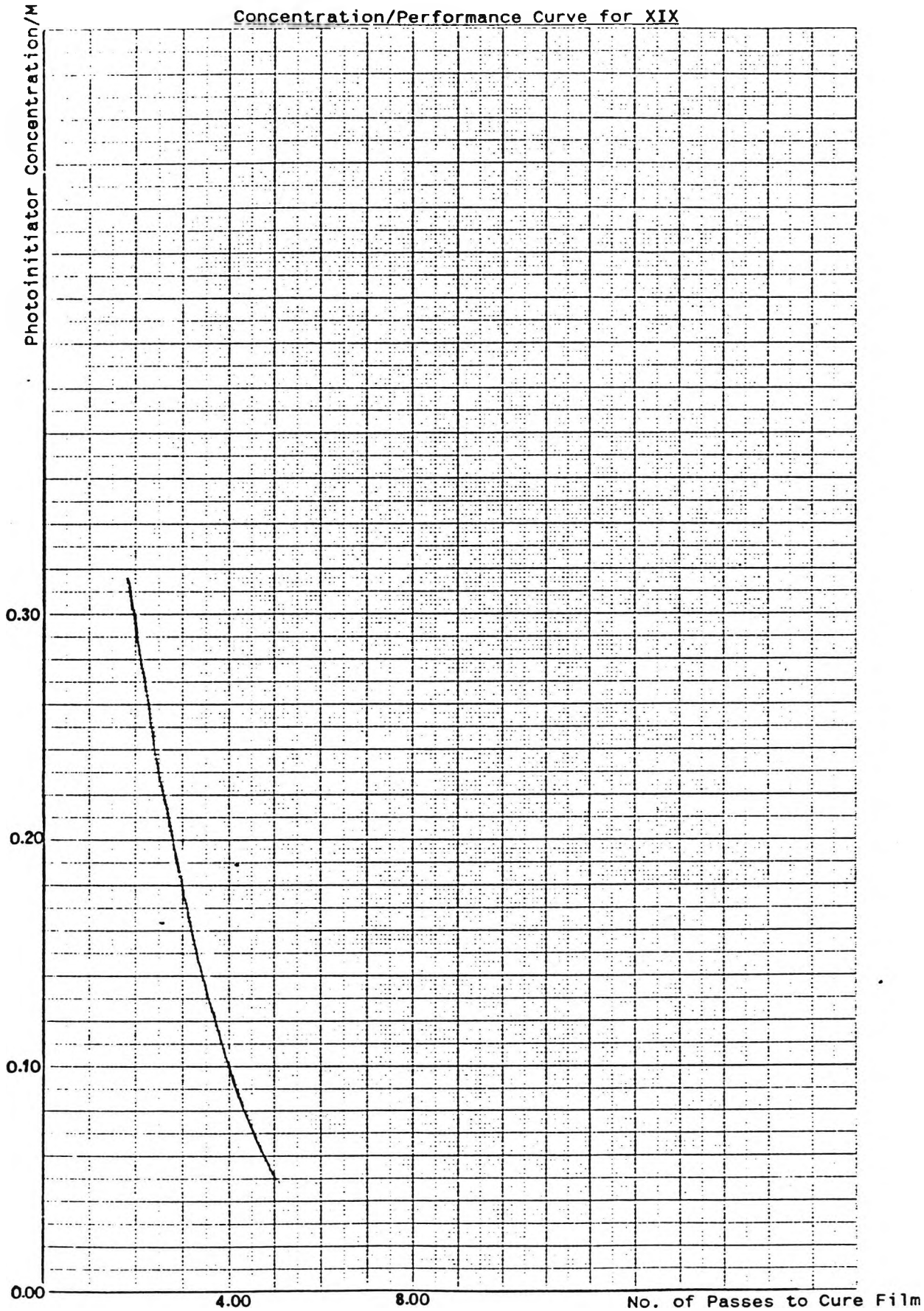
8.00
No. of Passes to Cure Fil


Concentration/Performance Curve for XIX
Photoinitiator Concentration/M
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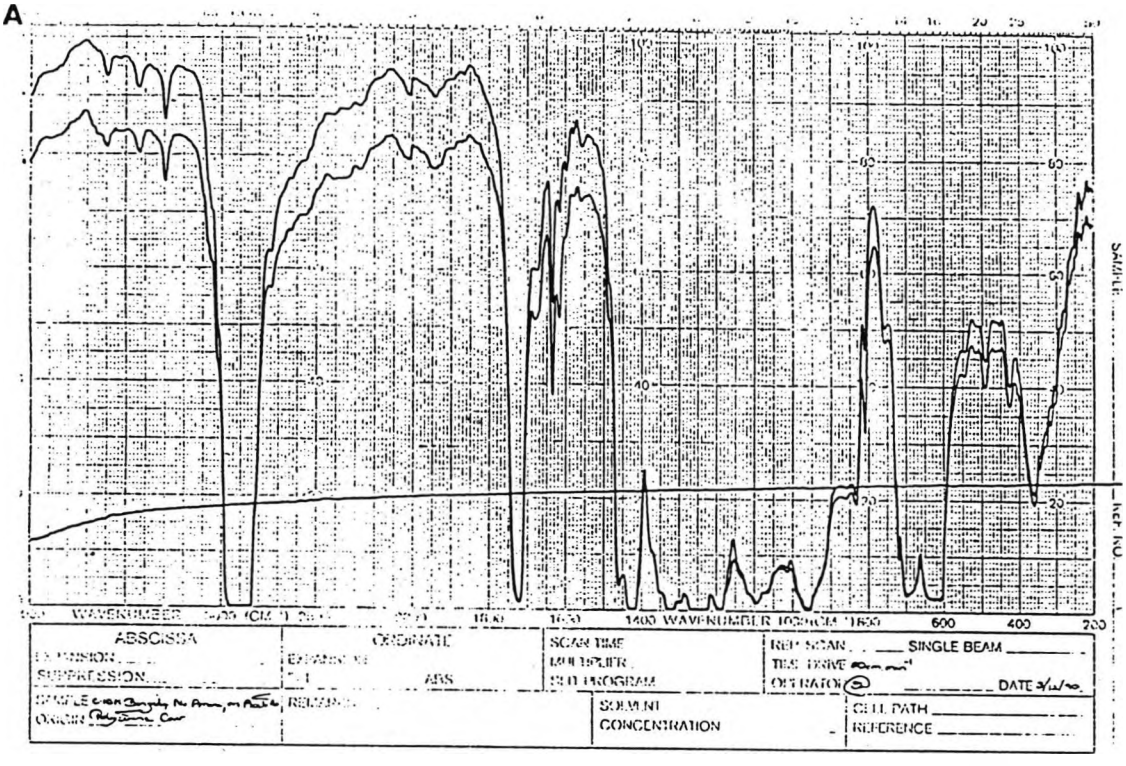
No. of Passes to Cure Film

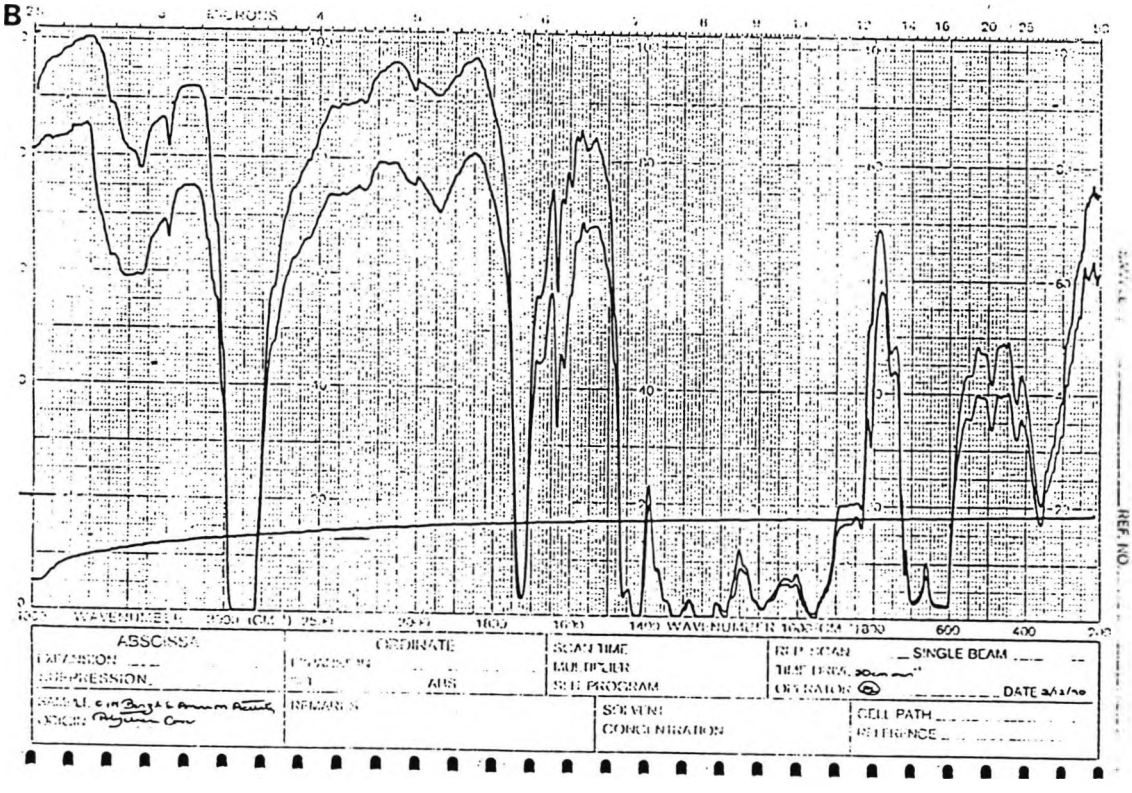
RTIR SPECTRA

I : Benzil

A


WAVENUMBER
1400 WAVENUMBER
600
400
200
ABSCISSA
ORDINATE
SCAN TIME
SINGLE BEAM
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REF. NO.

B


MICRONS
WAVENUMBER
1400 WAVENUMBER
600
400
ABSCISSA
ORDINATE
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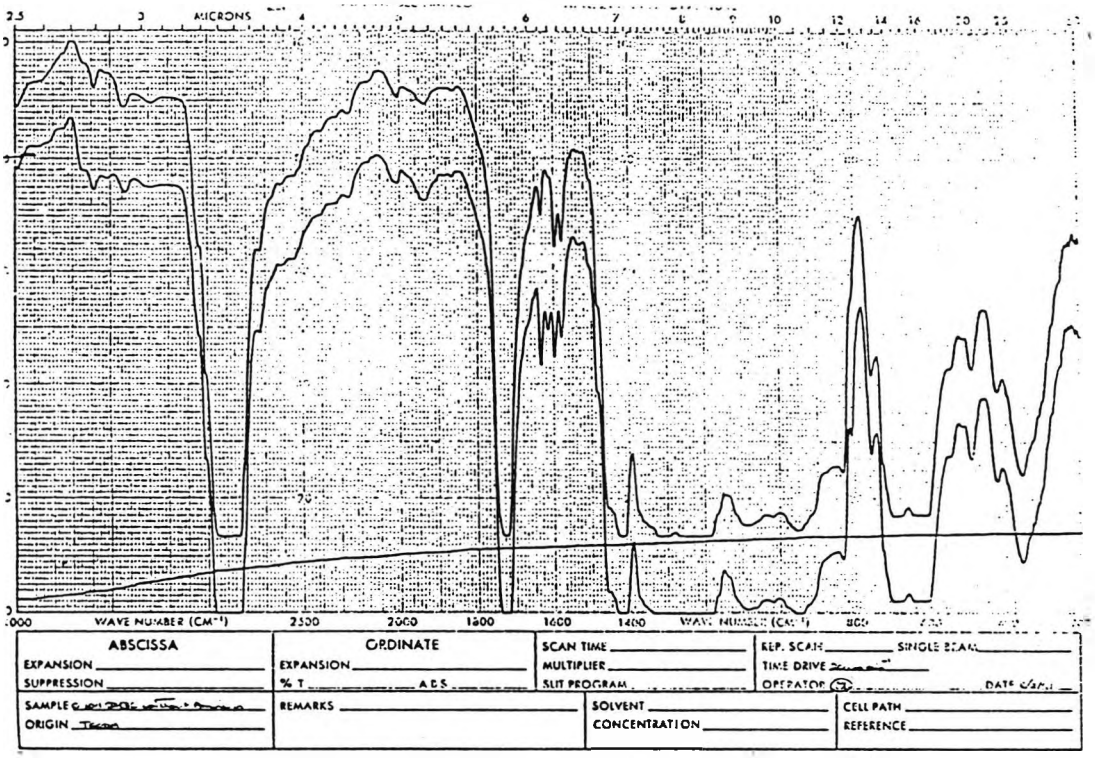
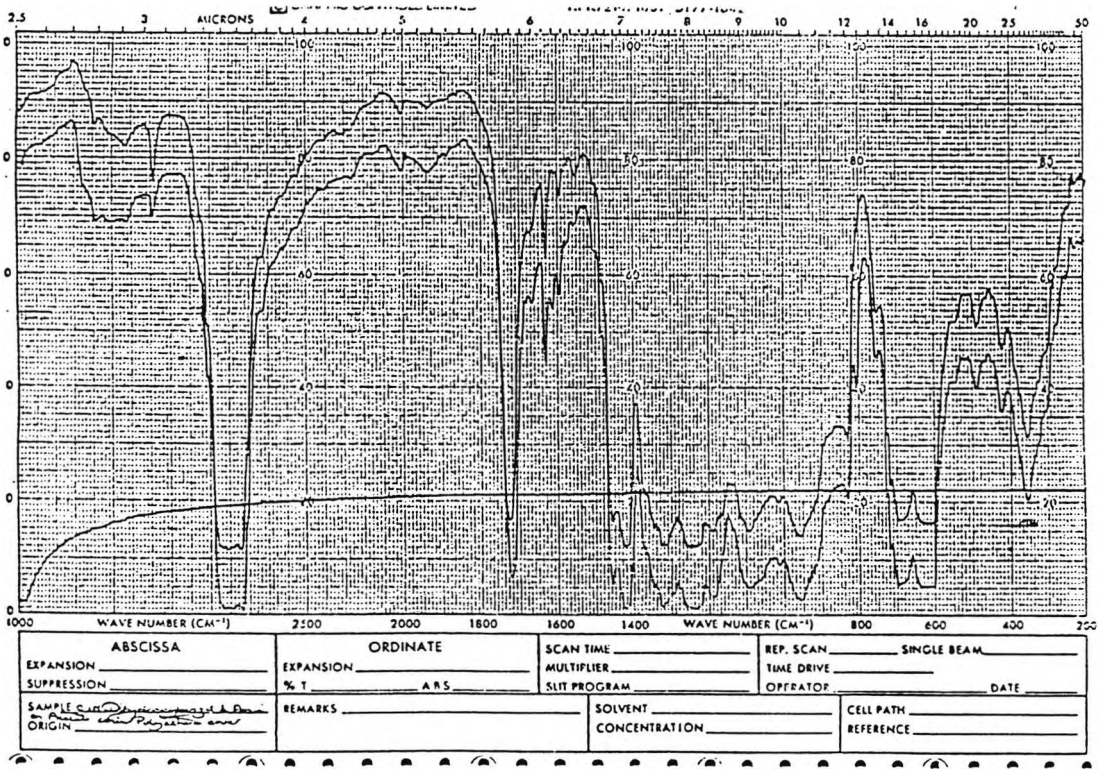
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REF. NO.

II : 4,4'-Dihydroxybenzil

A

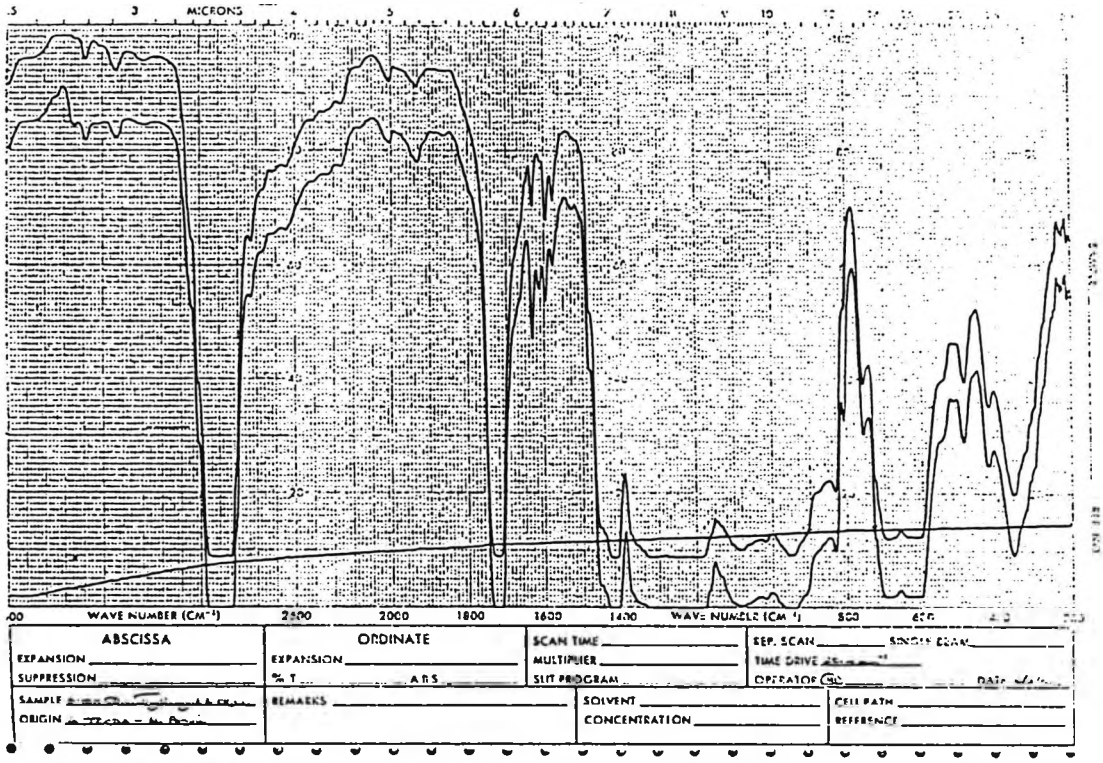


B

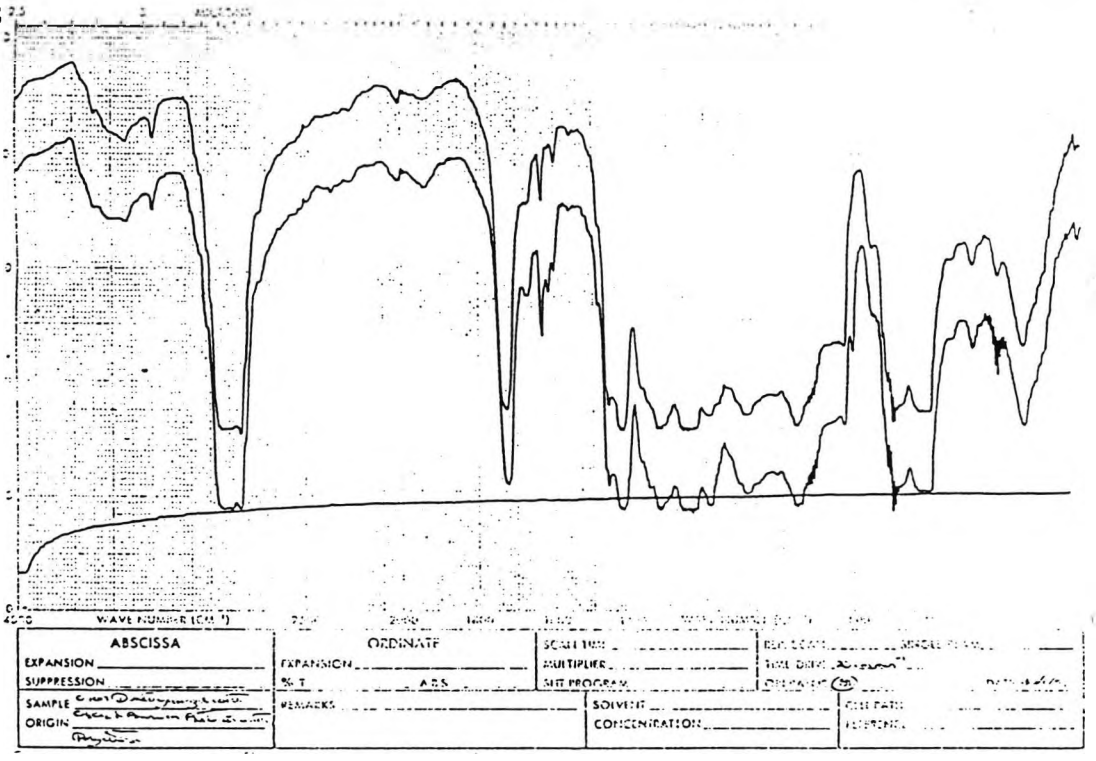


III : 4,4'-Dimethylbenzil

A



B



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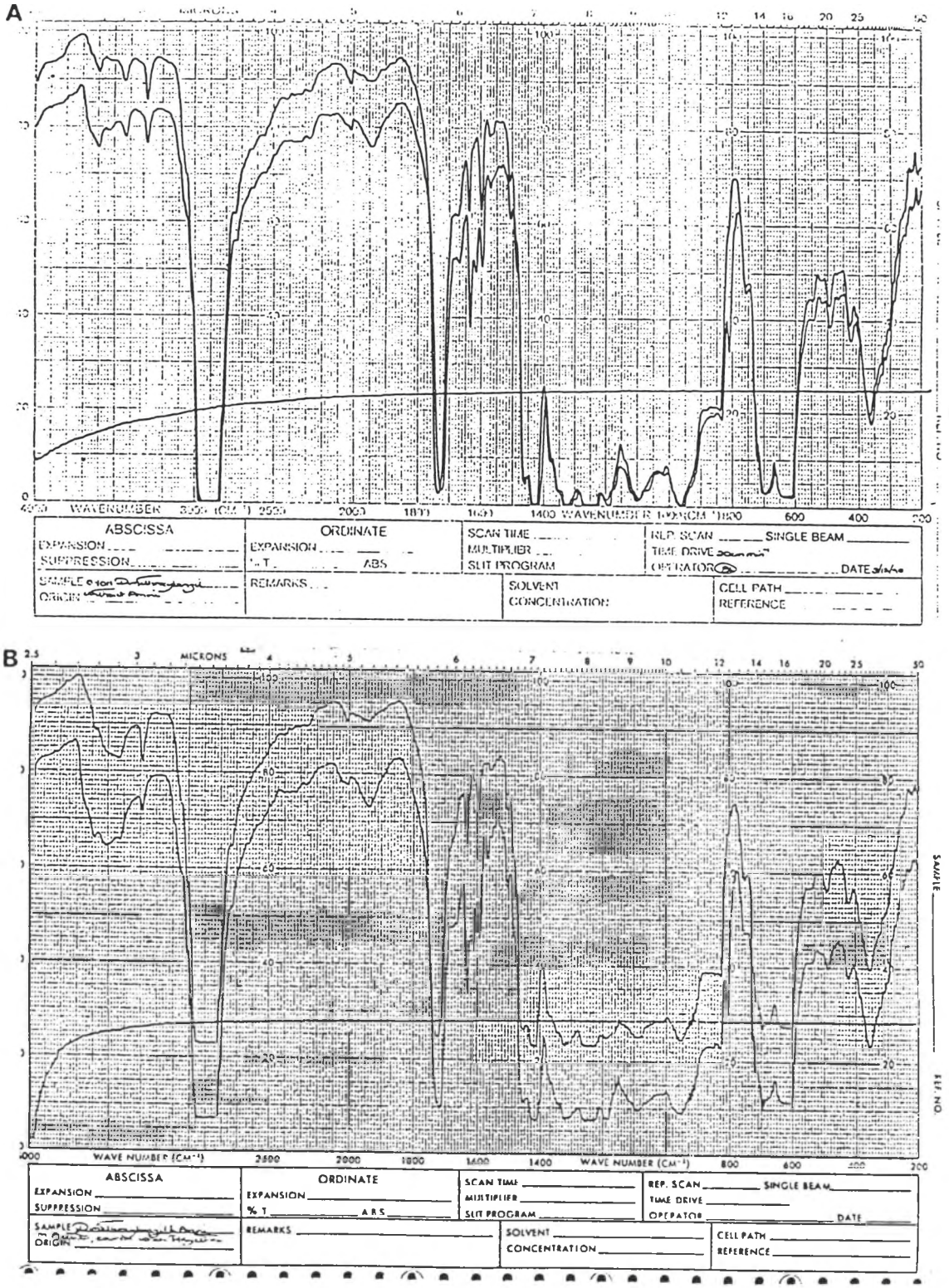

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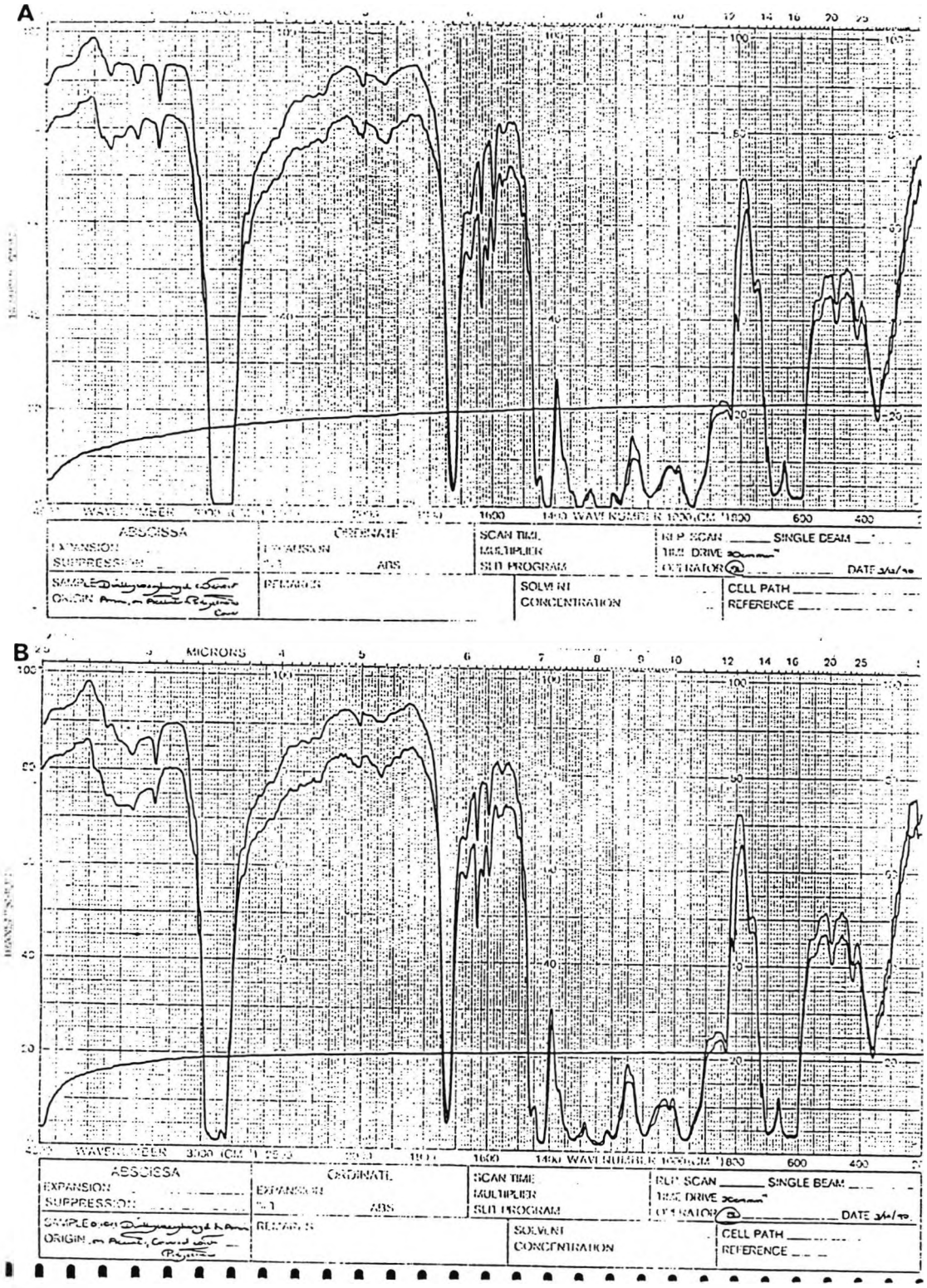
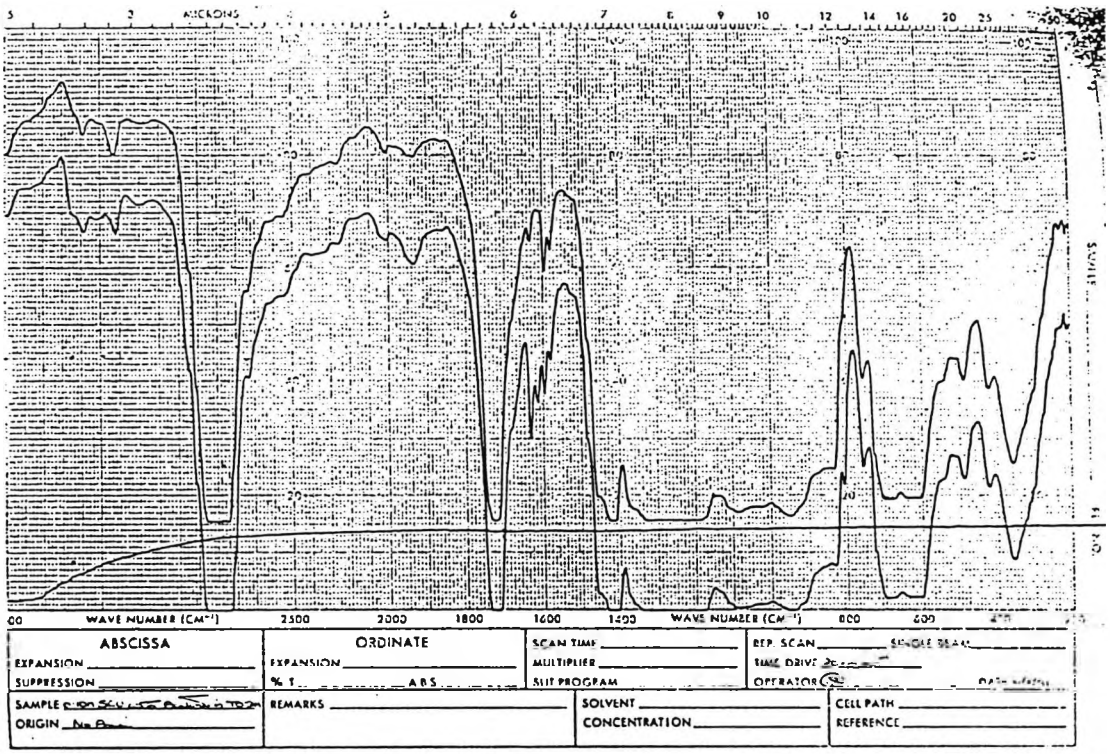


VI : Benzil-4,4'-Bis(n-Butyl Carbonate)

A



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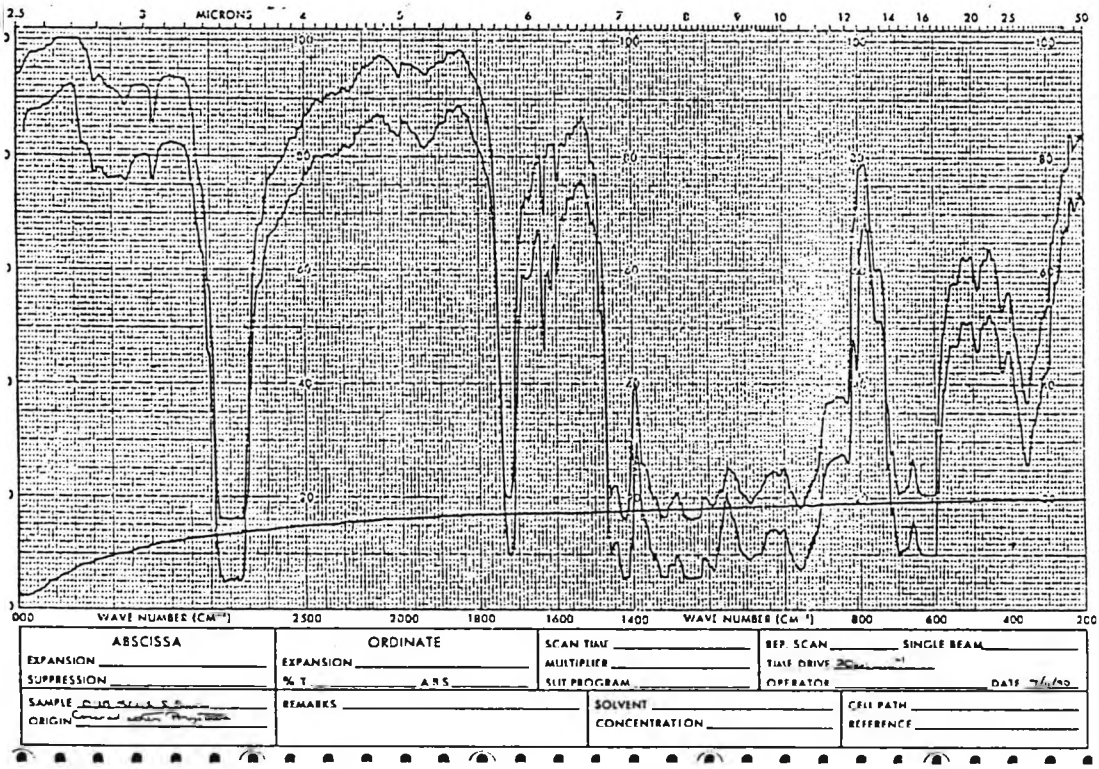
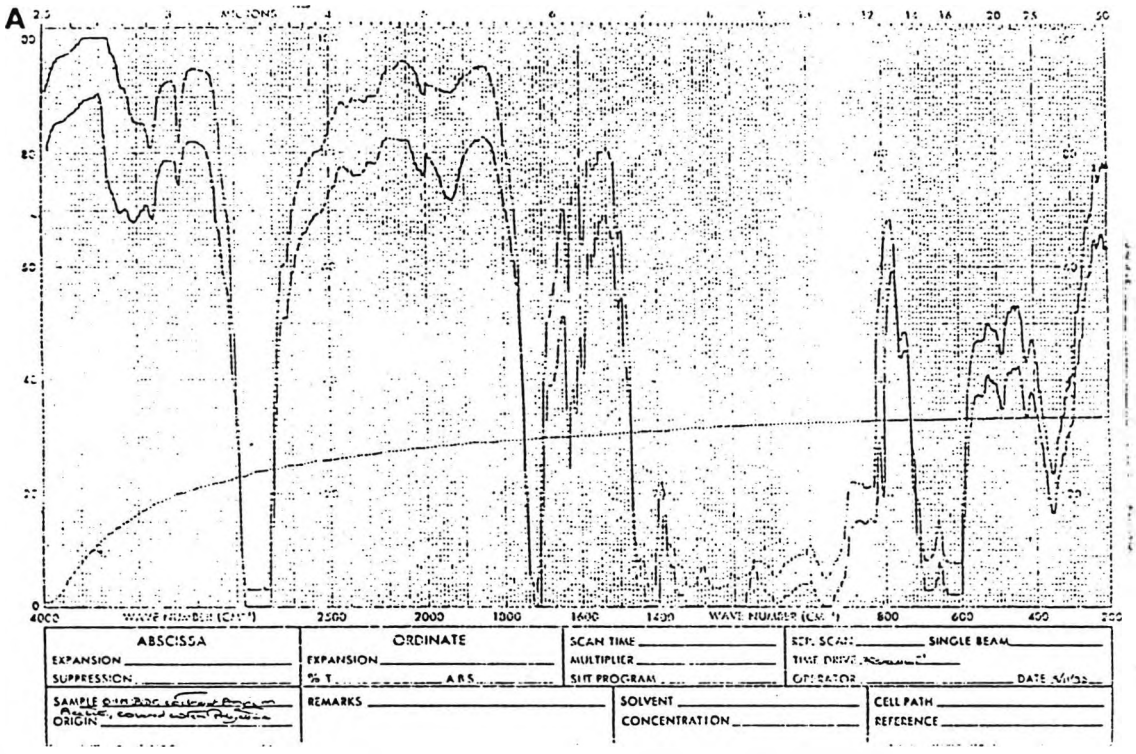
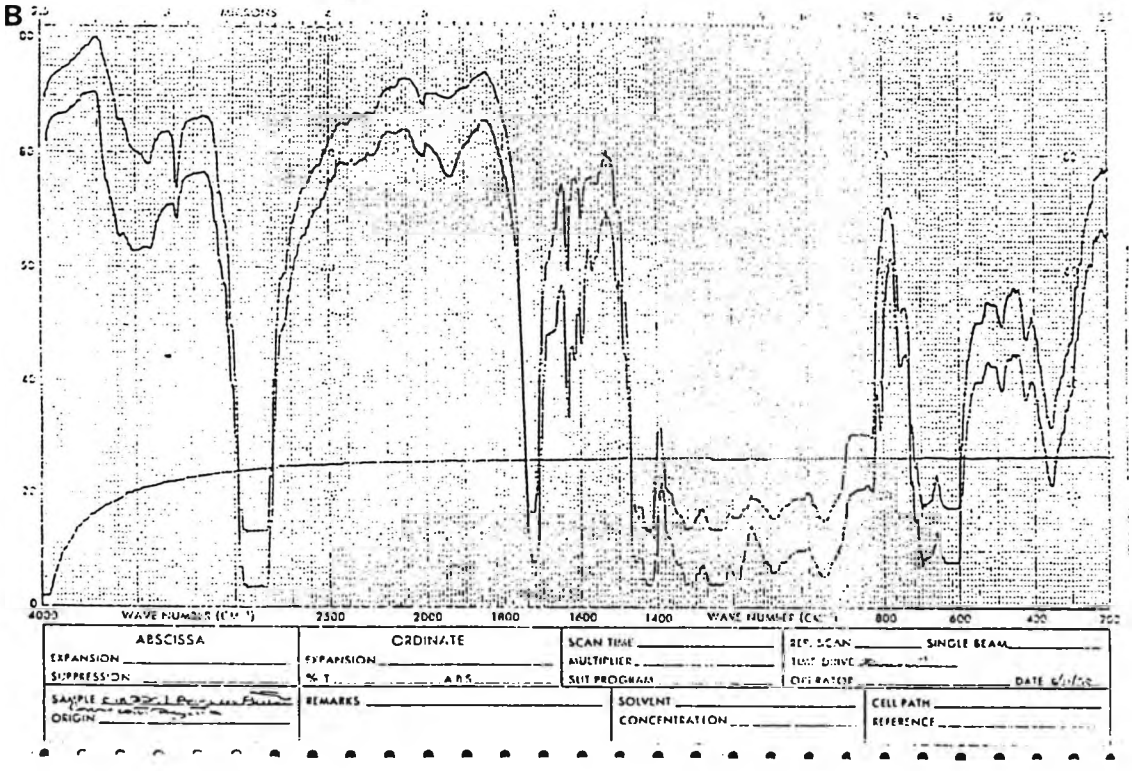


VII : Benzil-4,4'-Diglycidyl Ether





VIII : Bis[(2-Acrylate-3-Hydroxy)Propoxy] Benzil

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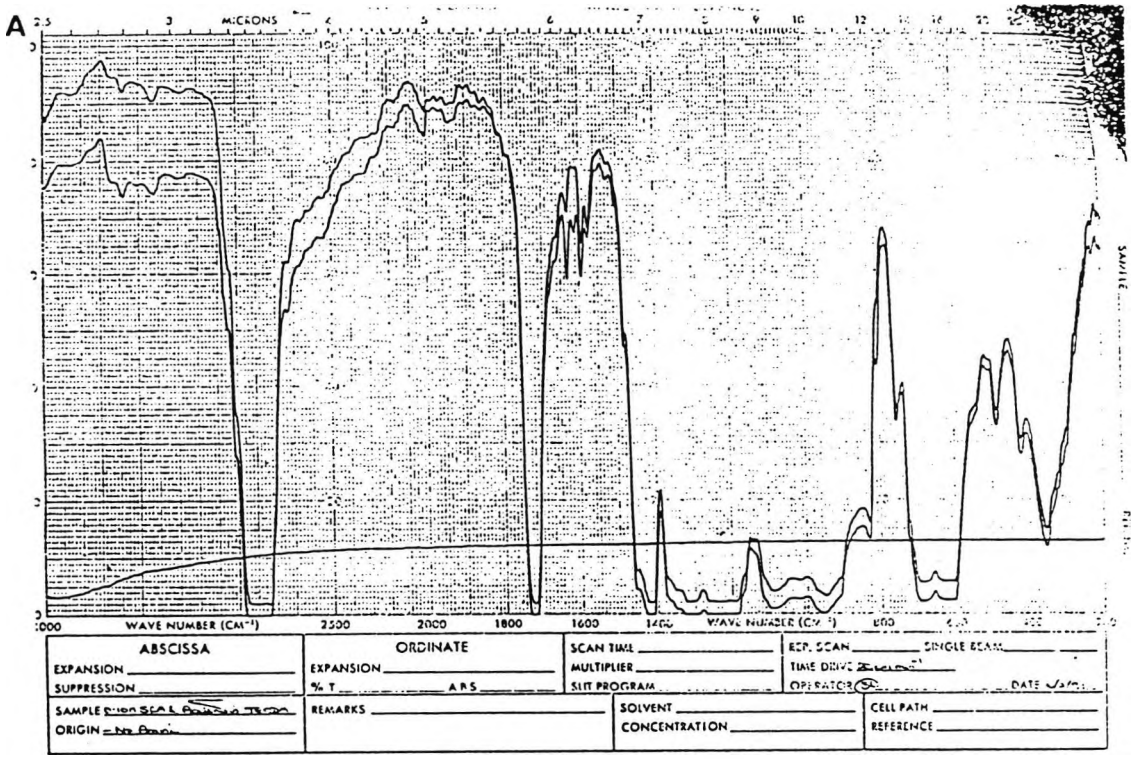

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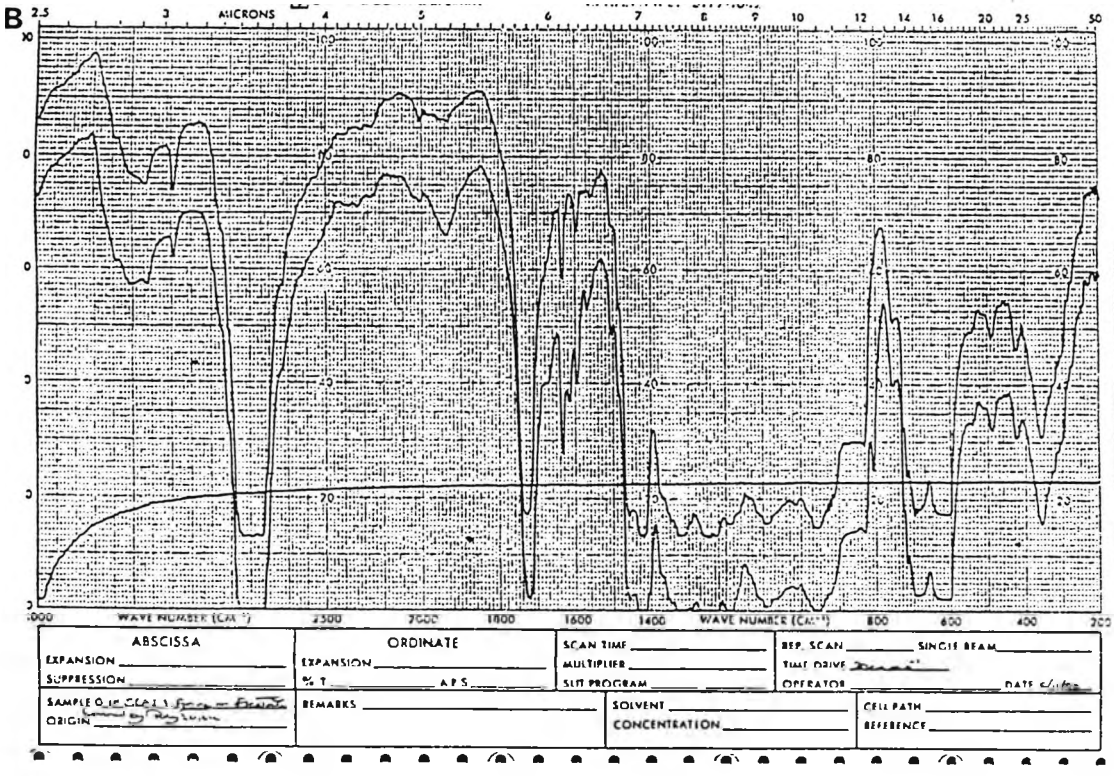
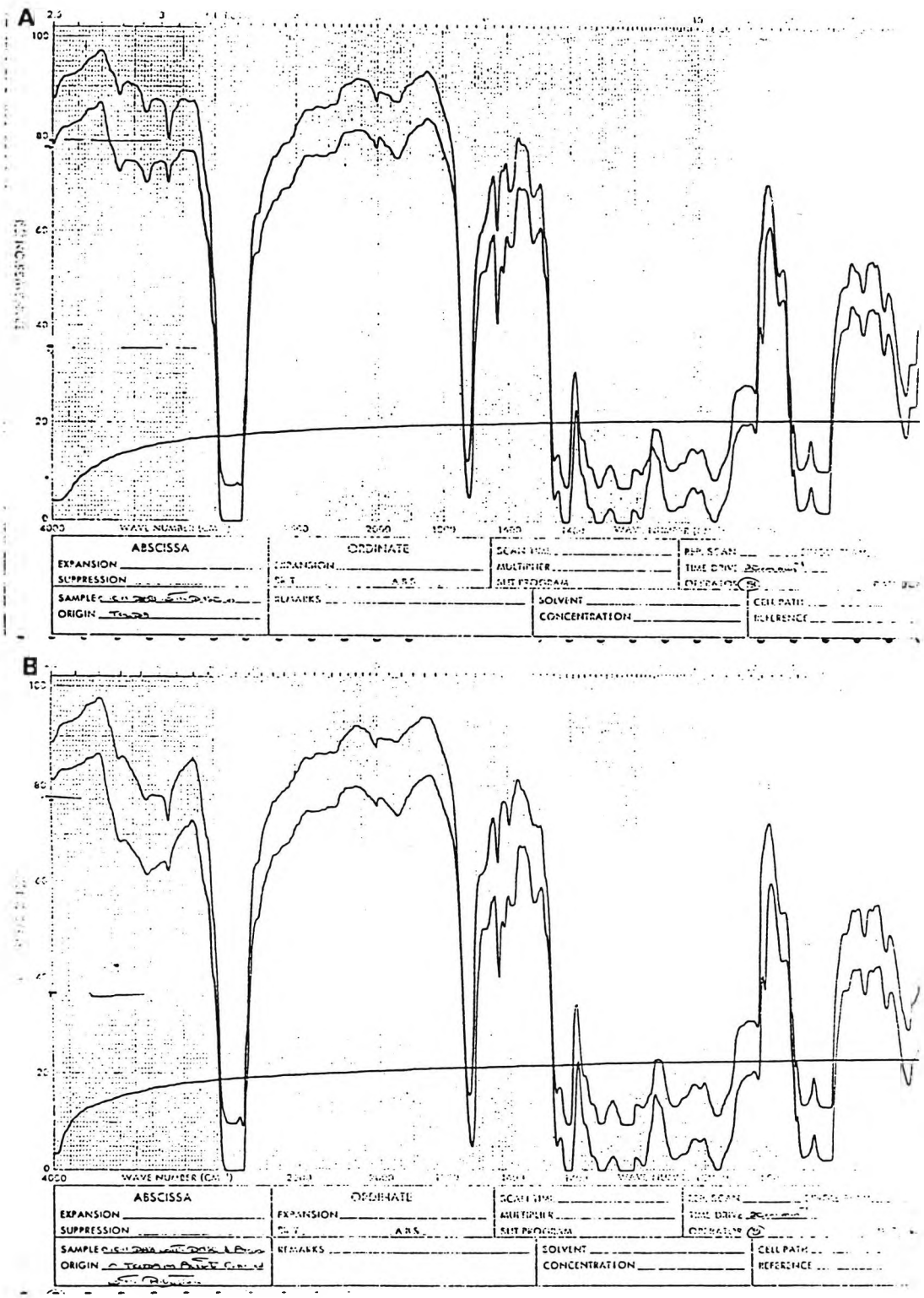
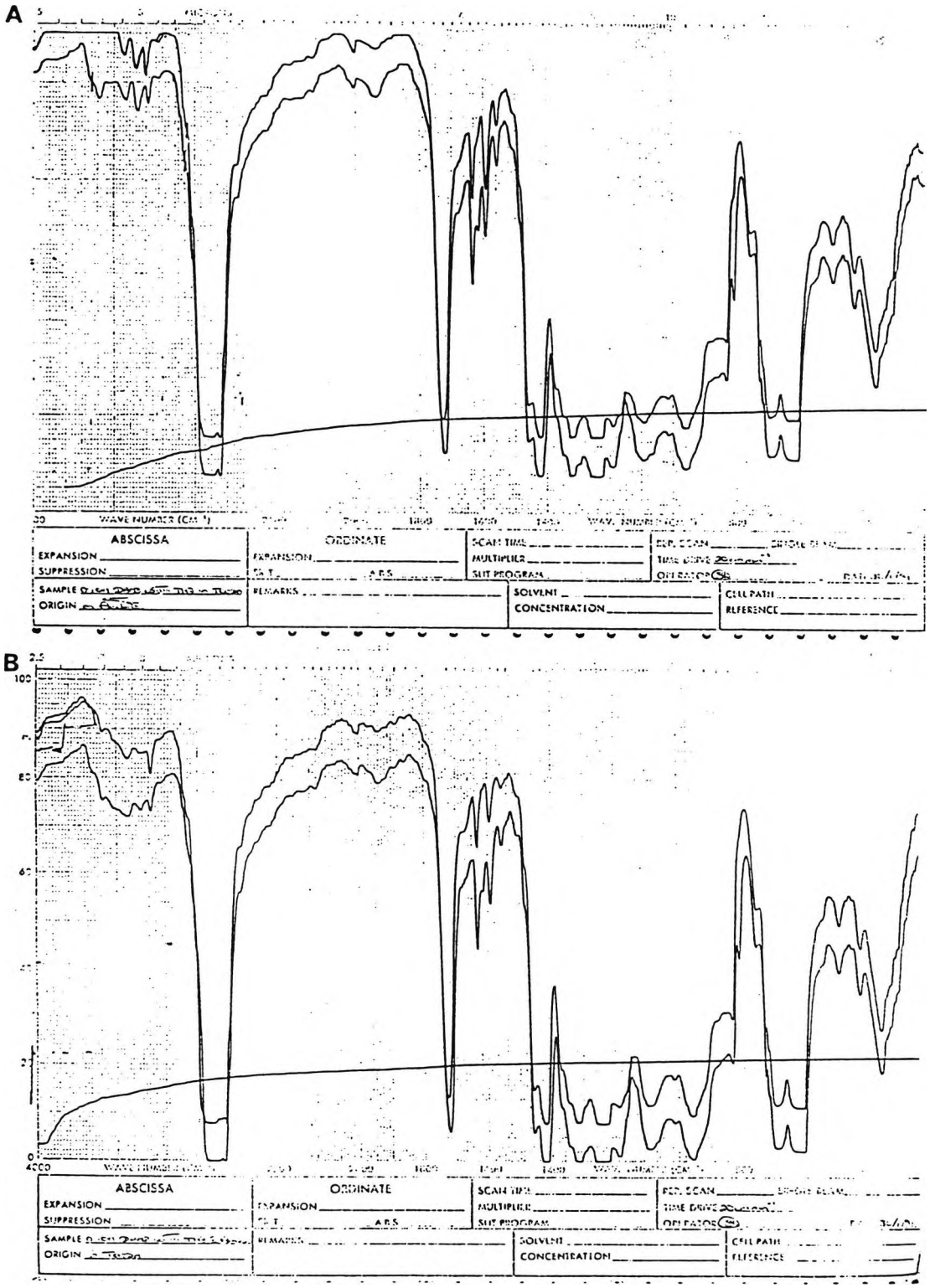


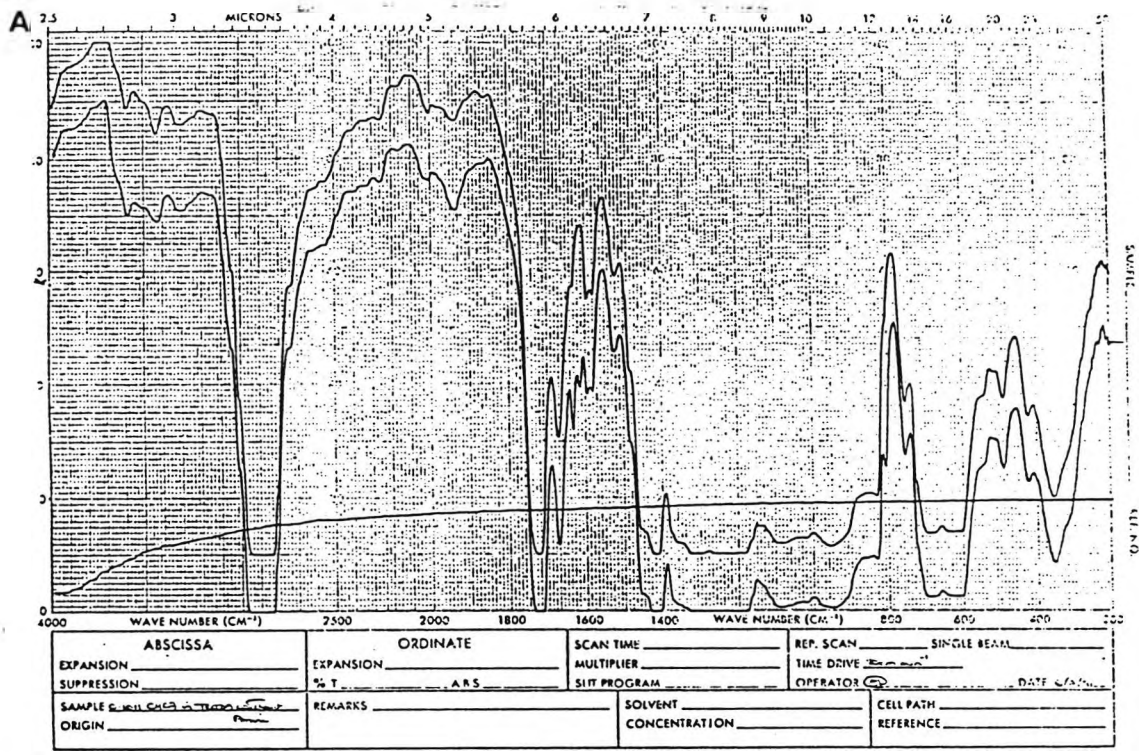
IX : 4,4'-Diacetamidobenzil

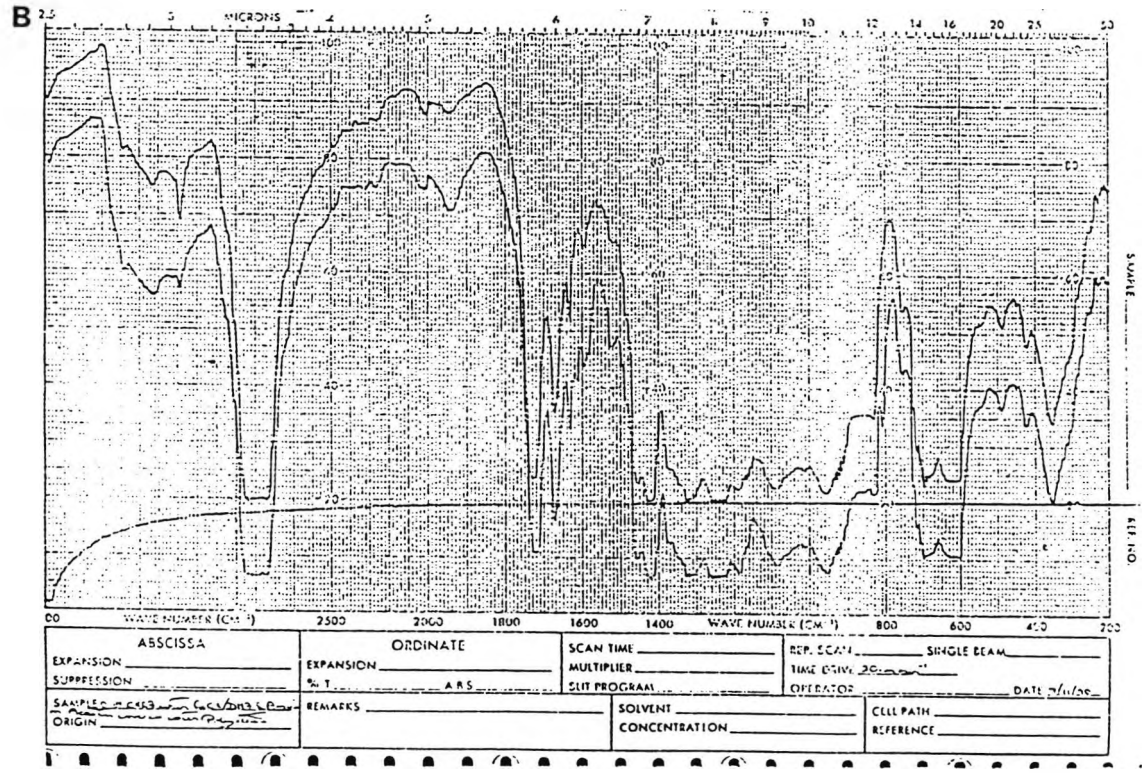


X : 4,4'-Diaminobenzil



XI : Benzil-4,4'-Bis(n-Butyl Urethane)





XII : Benzoin

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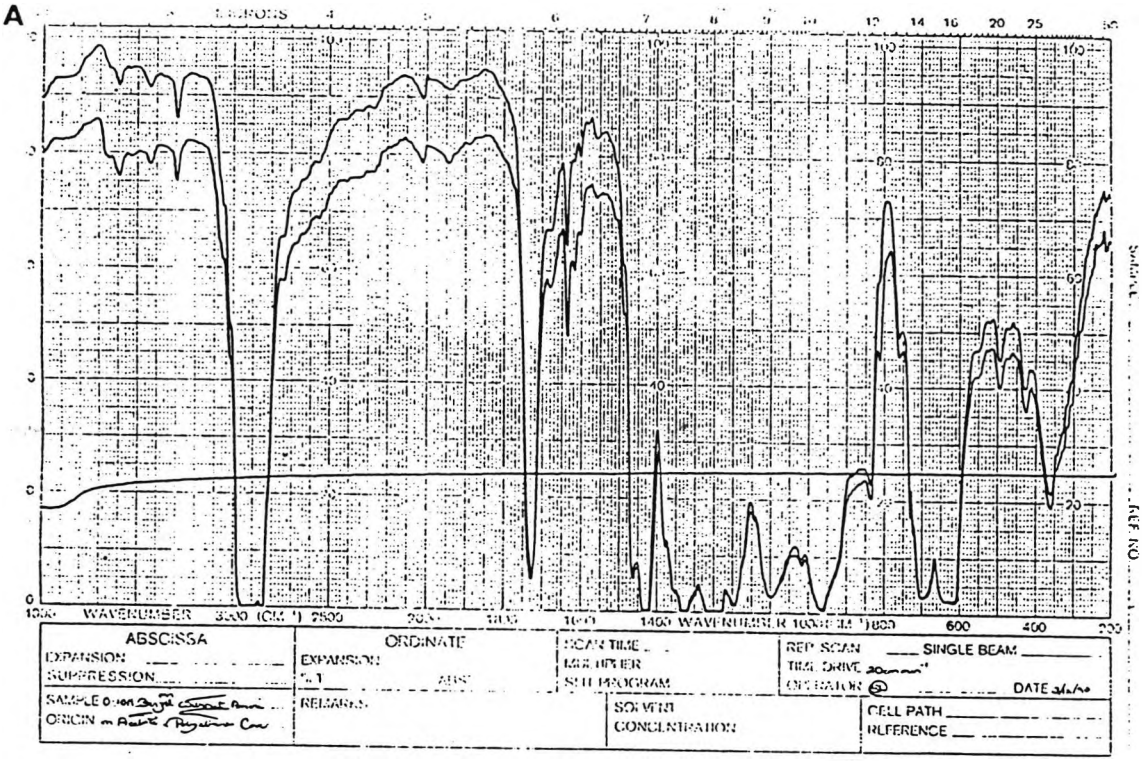

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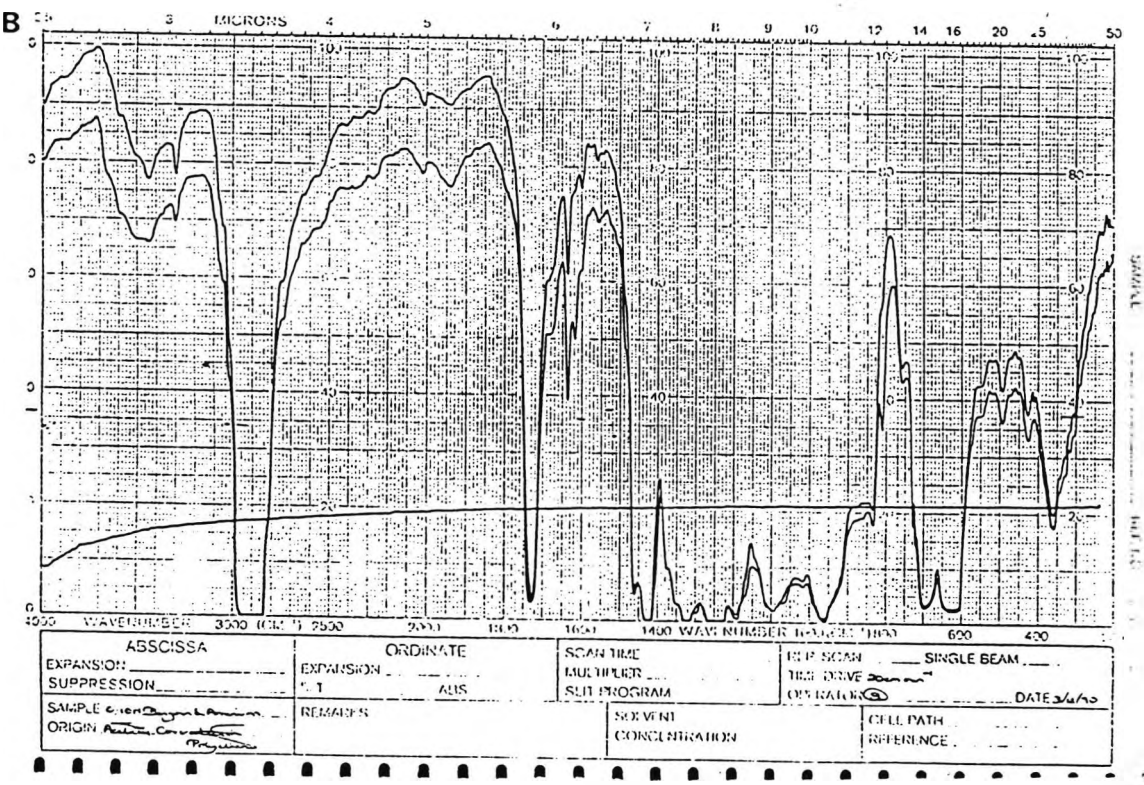
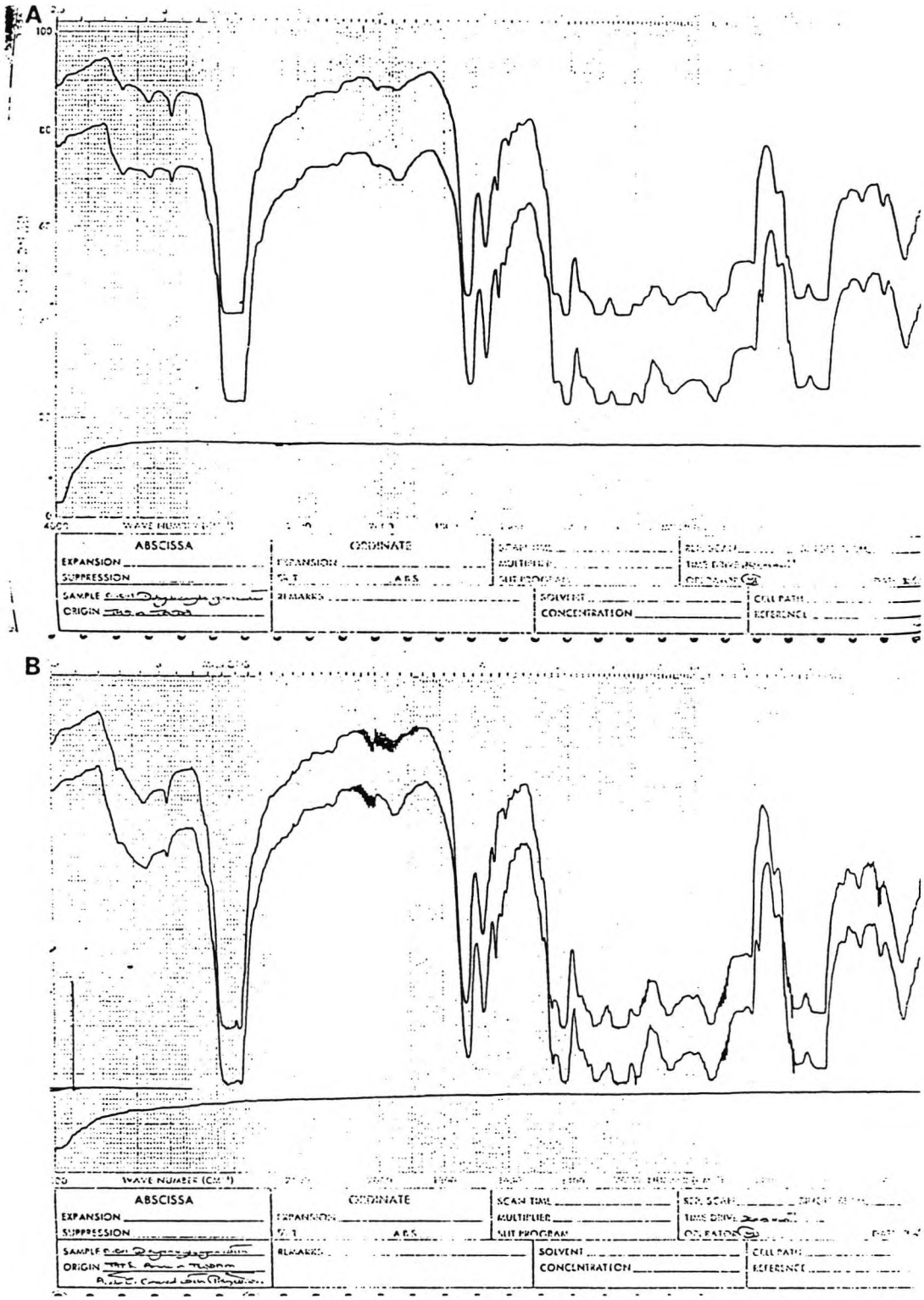


XIII : 4,4'-Dihydroxybenzoin



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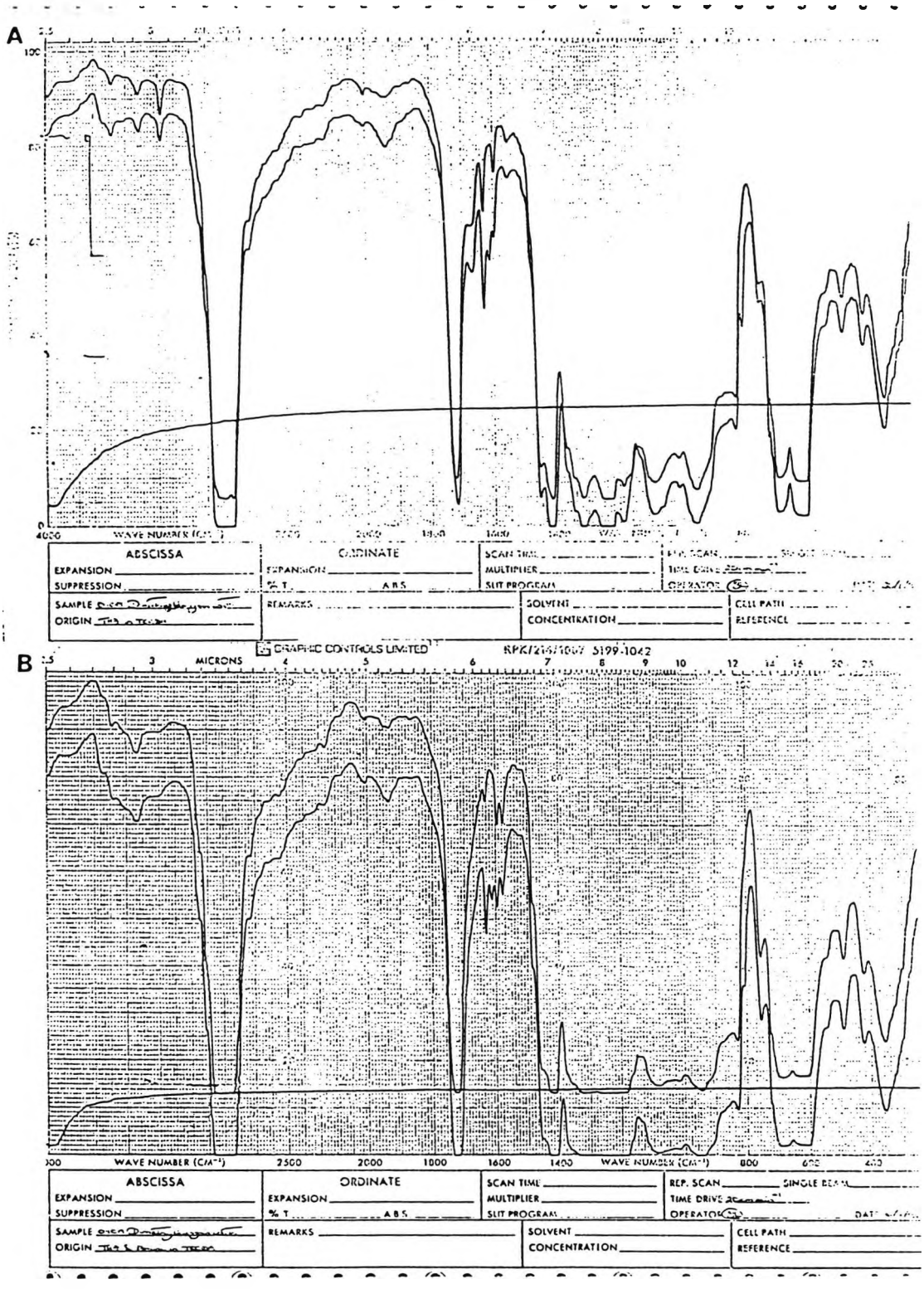

XV : 4,4'-Dimethoxybenzoin

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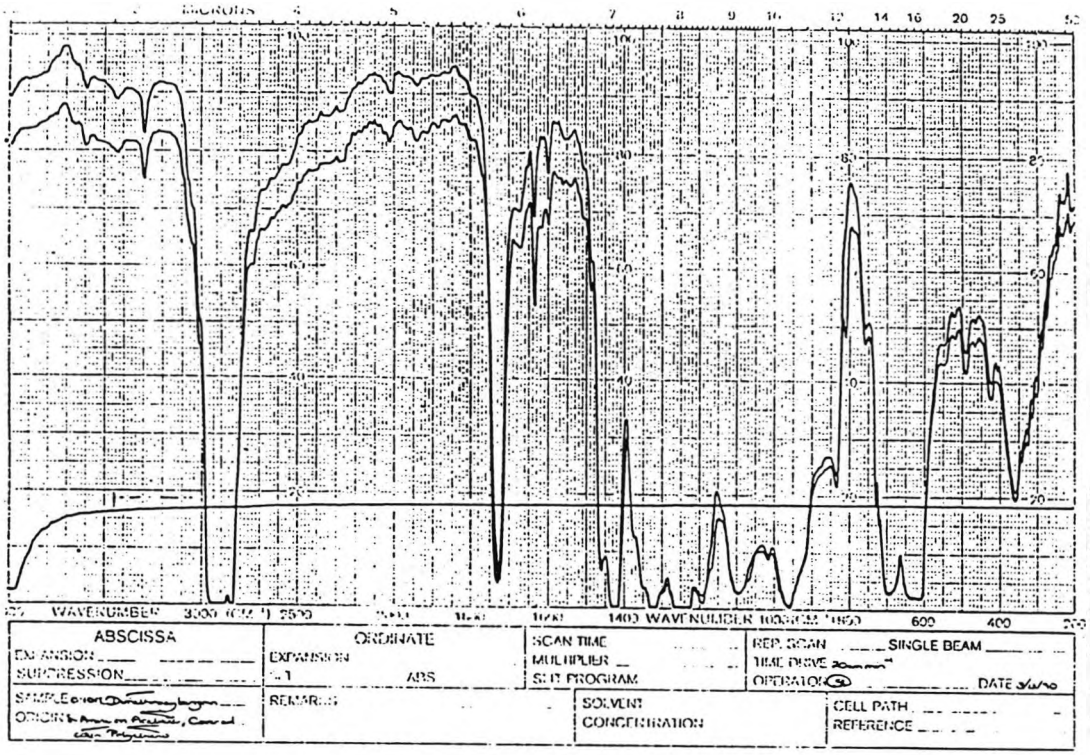

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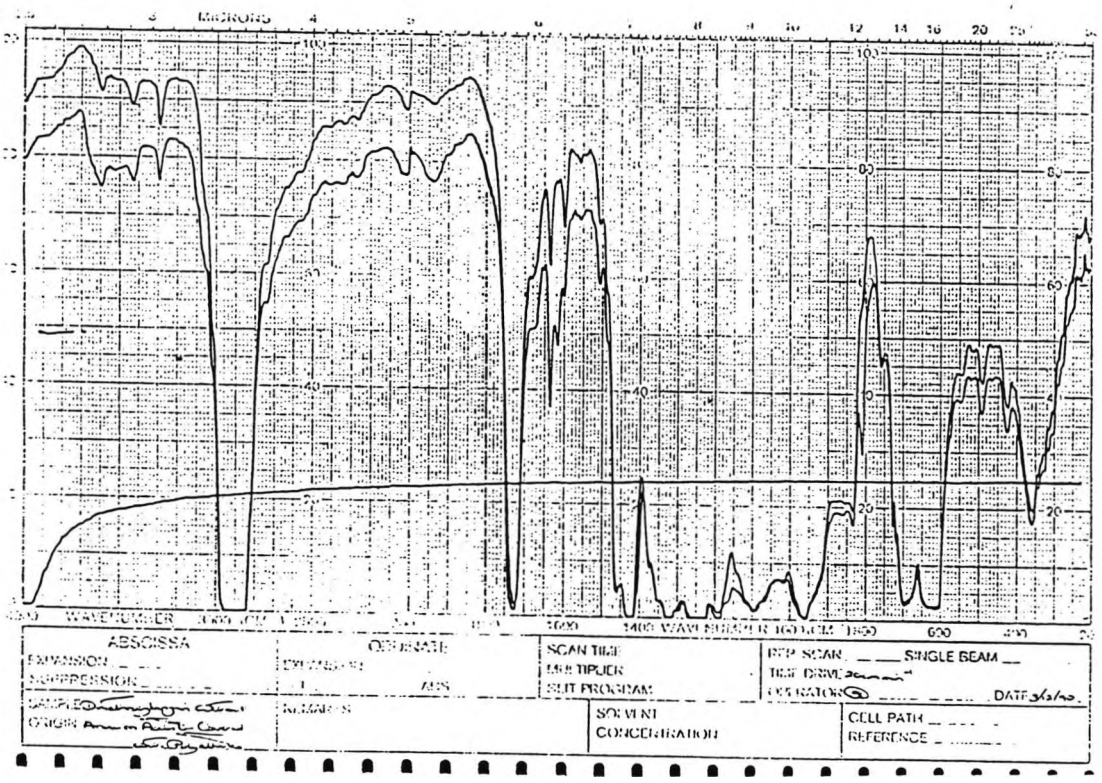
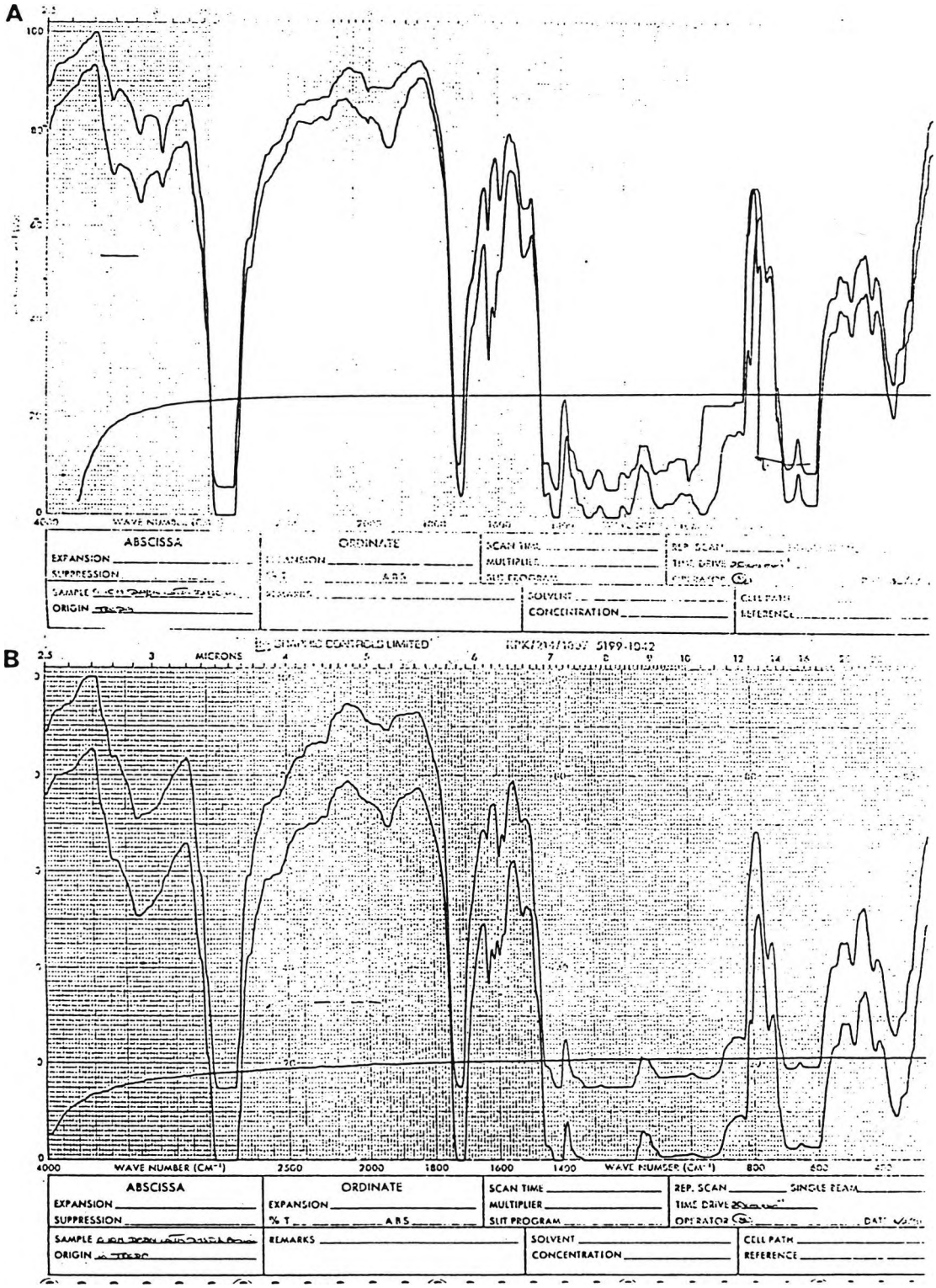
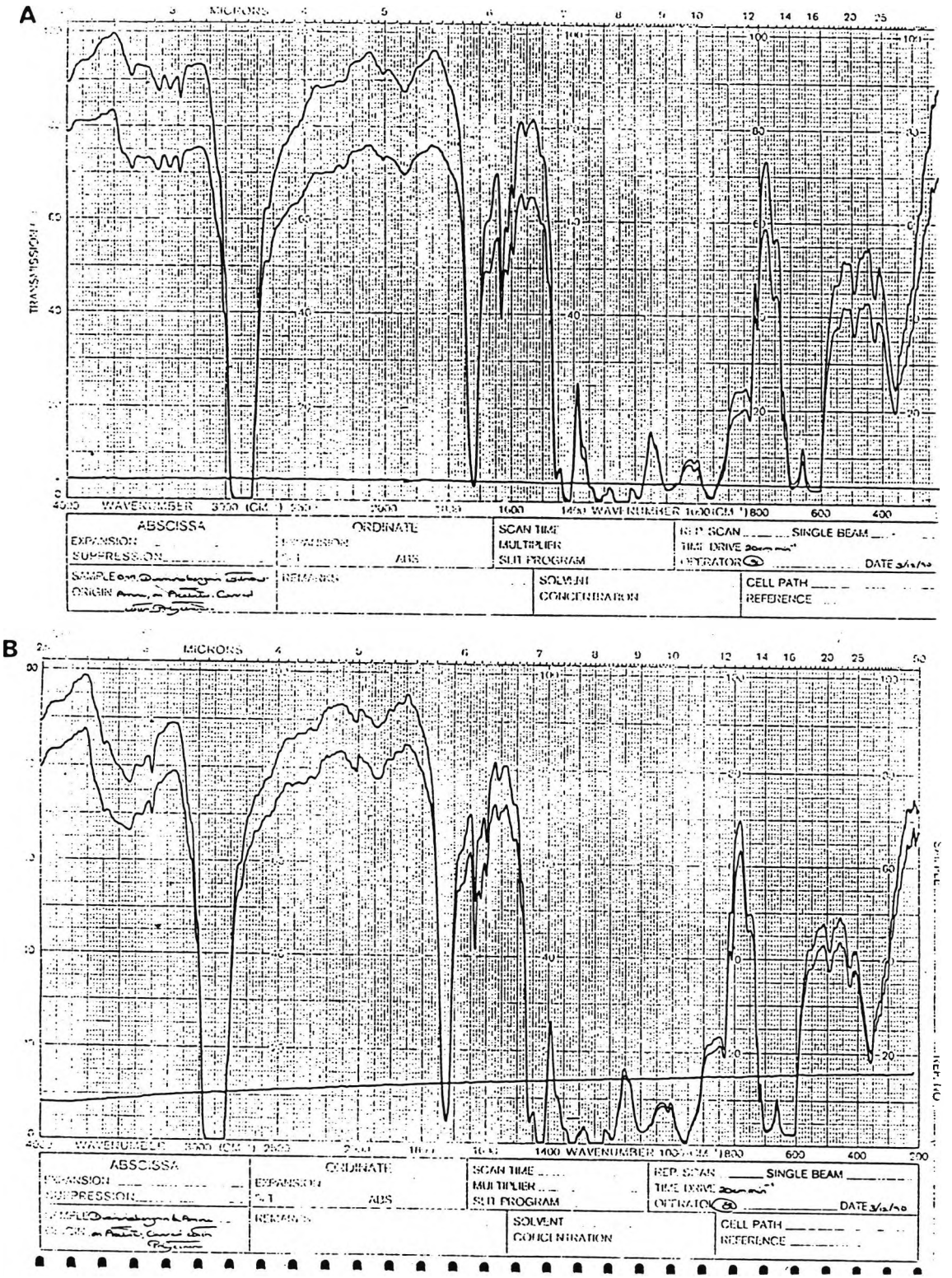


XIX : 4,4'-Diacetamidobenzoin



XX : 4,4'-Diaminobenzoin



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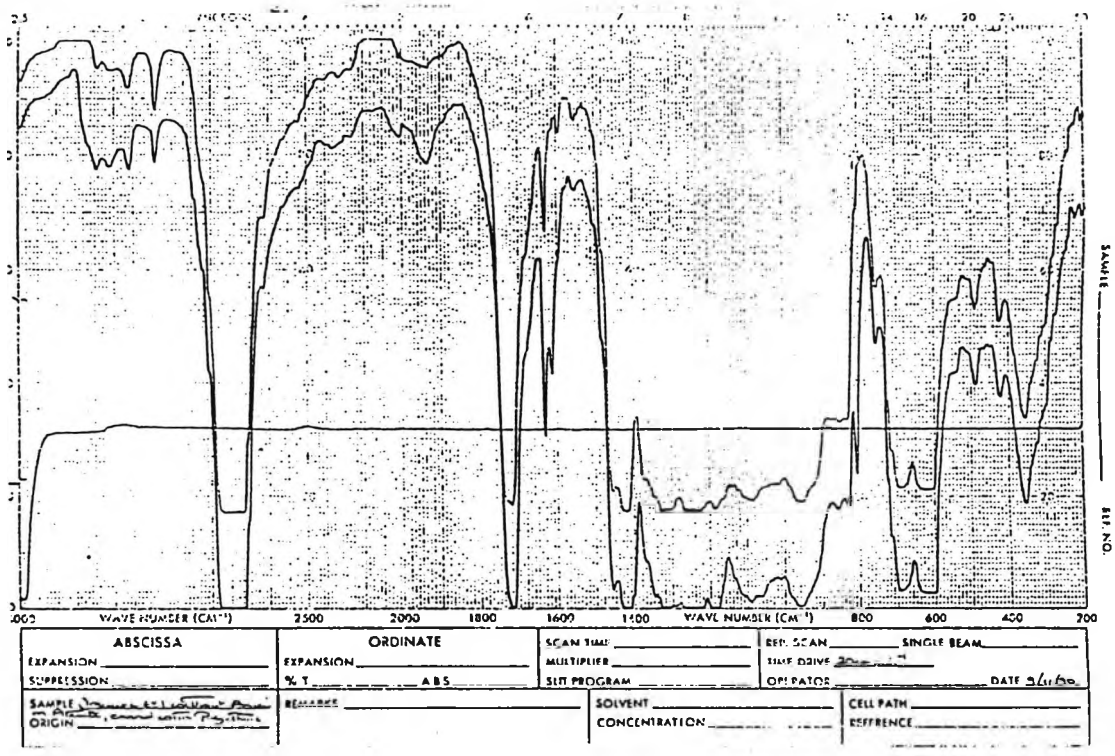

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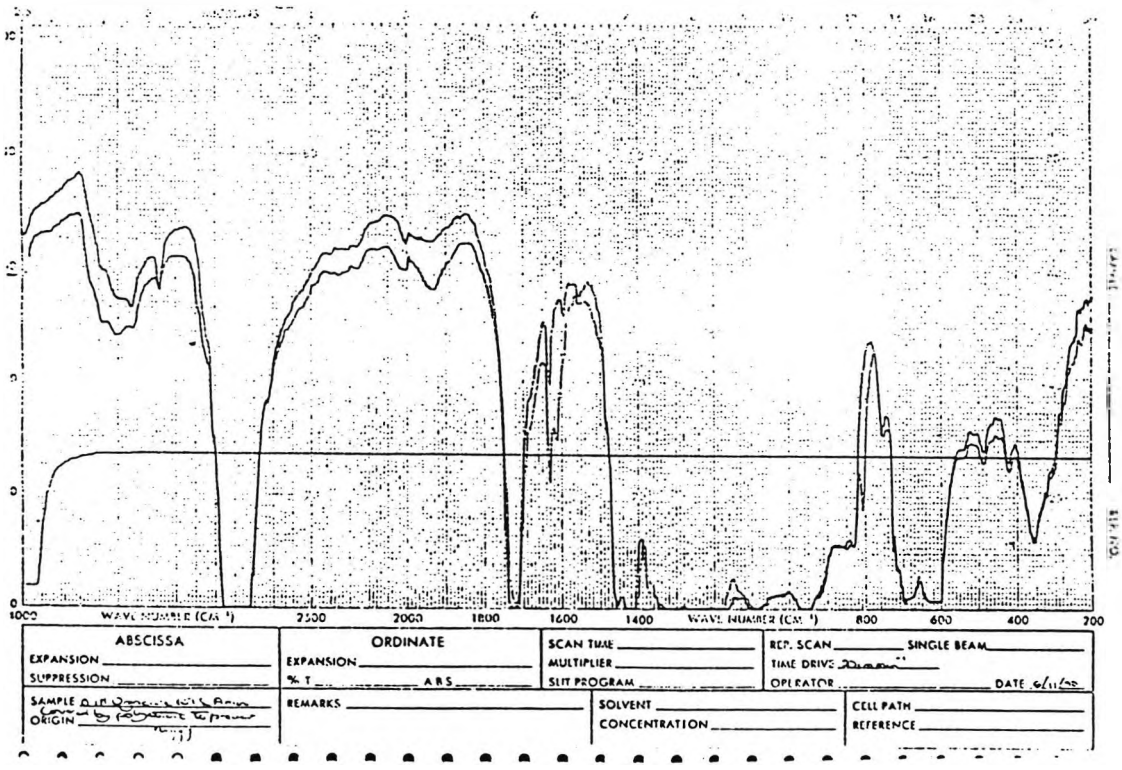


APPENDIX IV:

SUPPLEMENTARY DATA

TO

CHAPTER VI

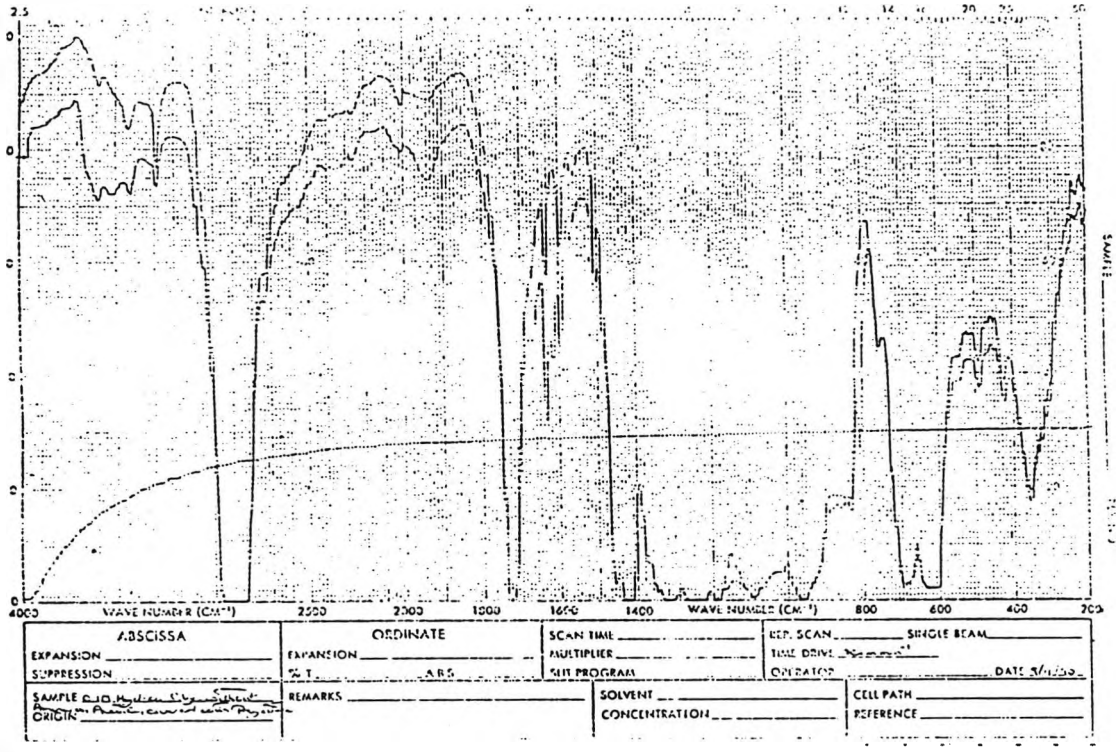
RTIR SPECTRA

Key to Symbols

Symbol	Monomers from which Copolymers Formed
GLYC	Benzil-4,4'-Diglycidyl Ether & 5,5-Dimethylhydantoin
HIS	4,4'-Dihydroxybenzil & Isophorone Diisocyanate
HDI	4,4'-Dihydroxybenzil & 1,6-Diisocyanatohexane

GLYC

A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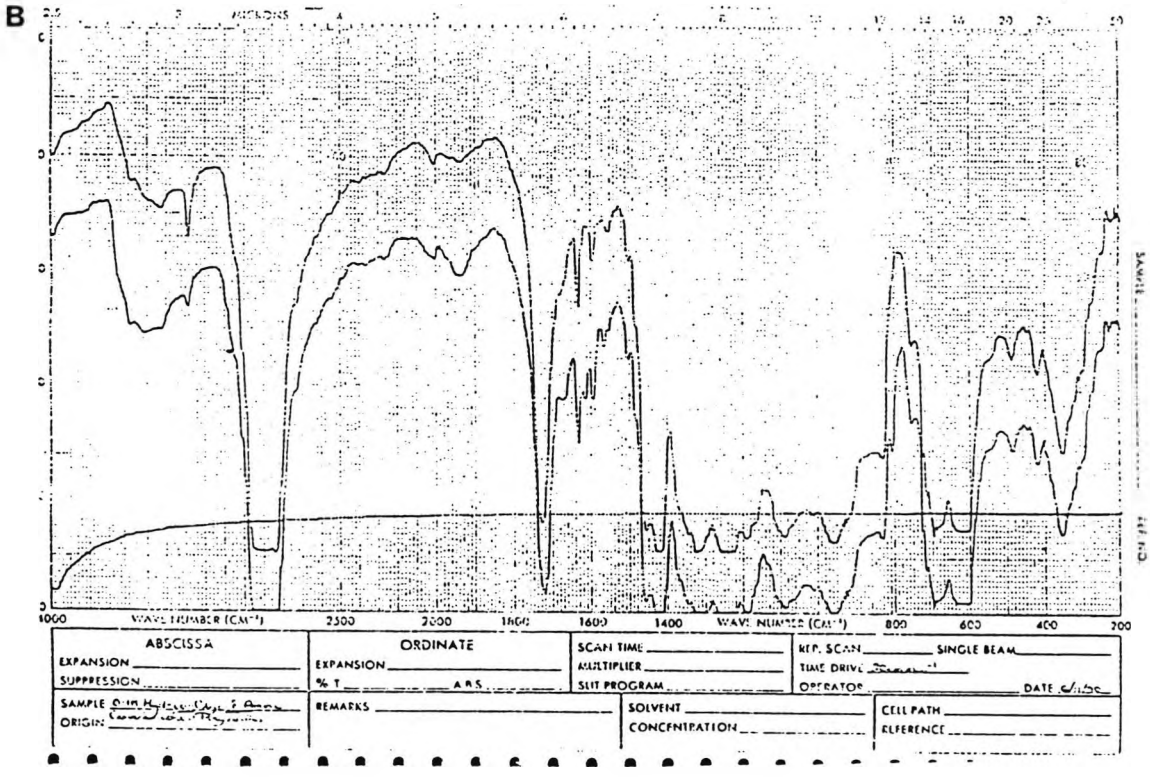
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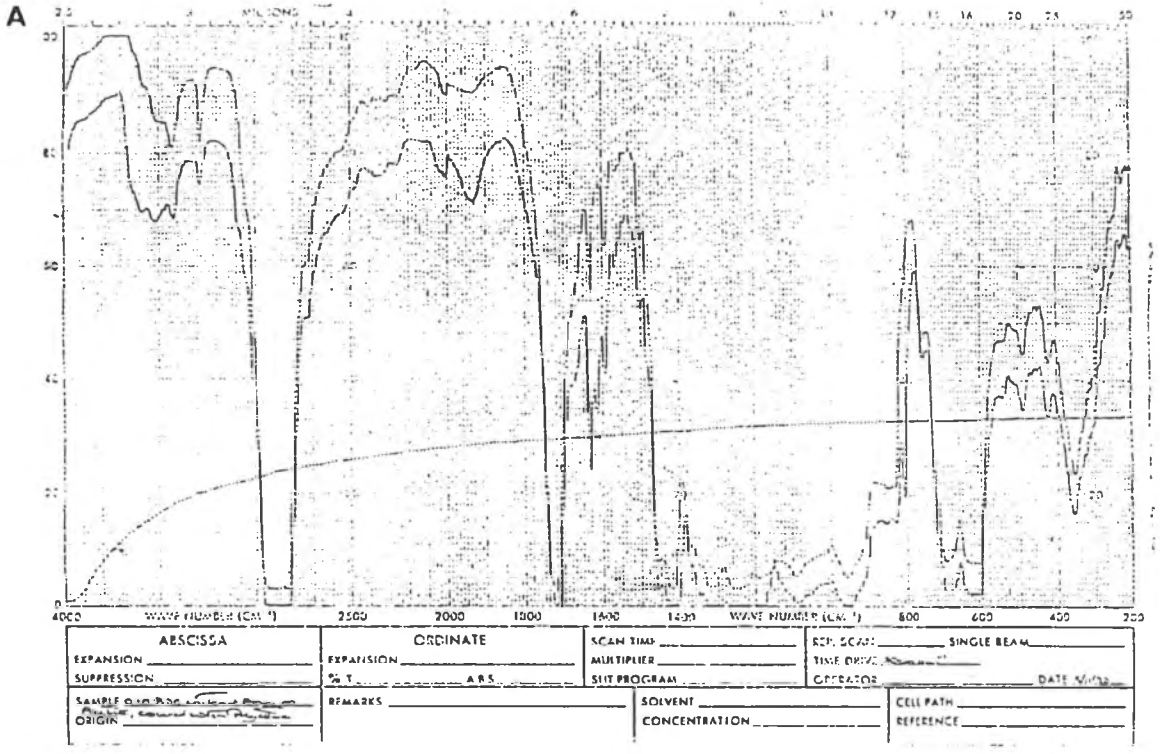
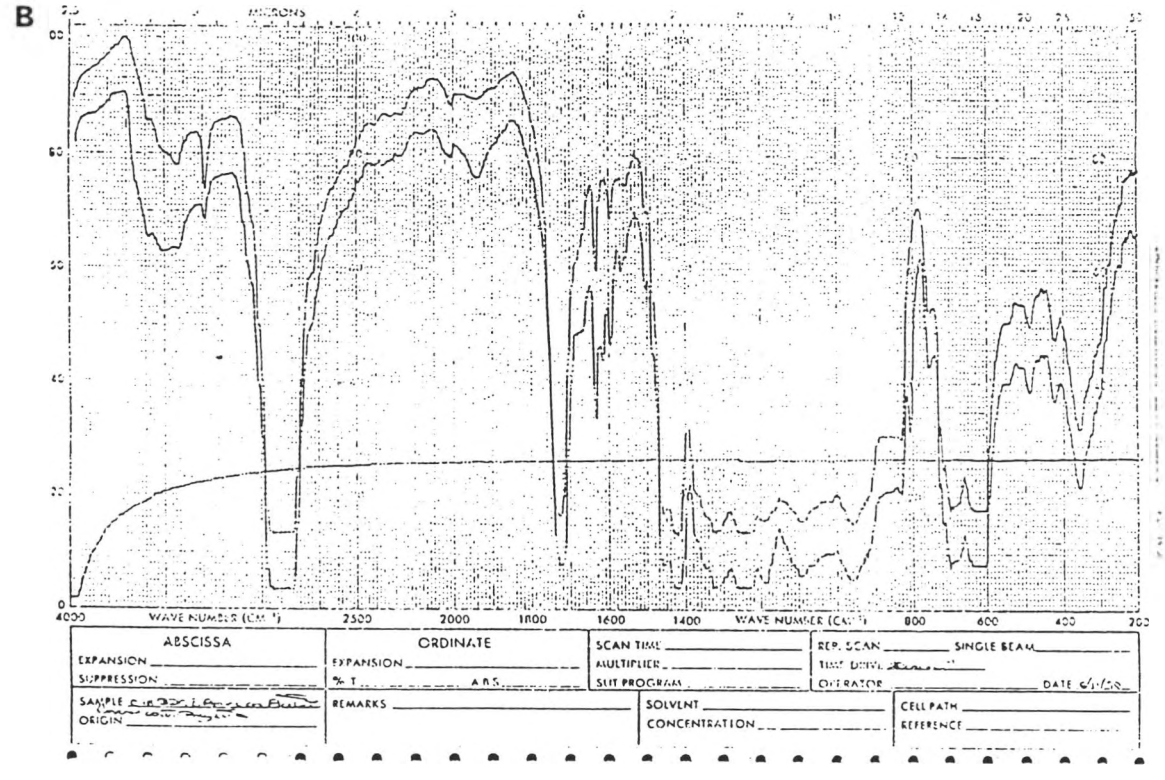
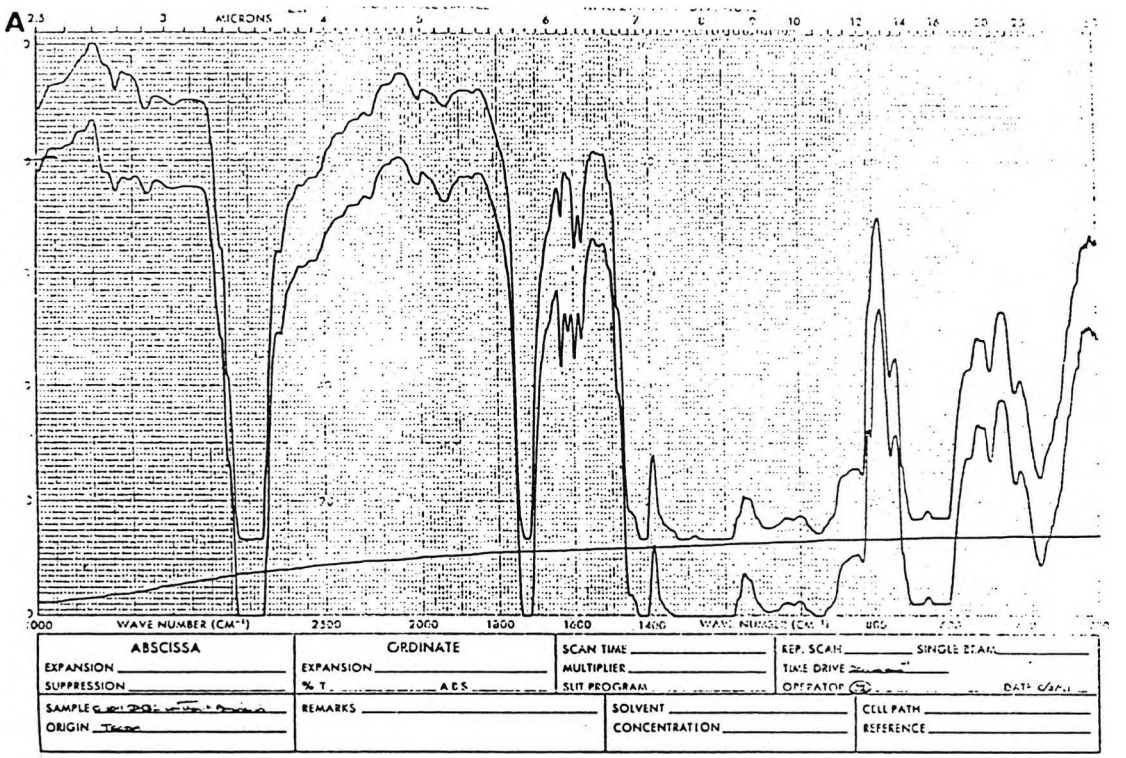
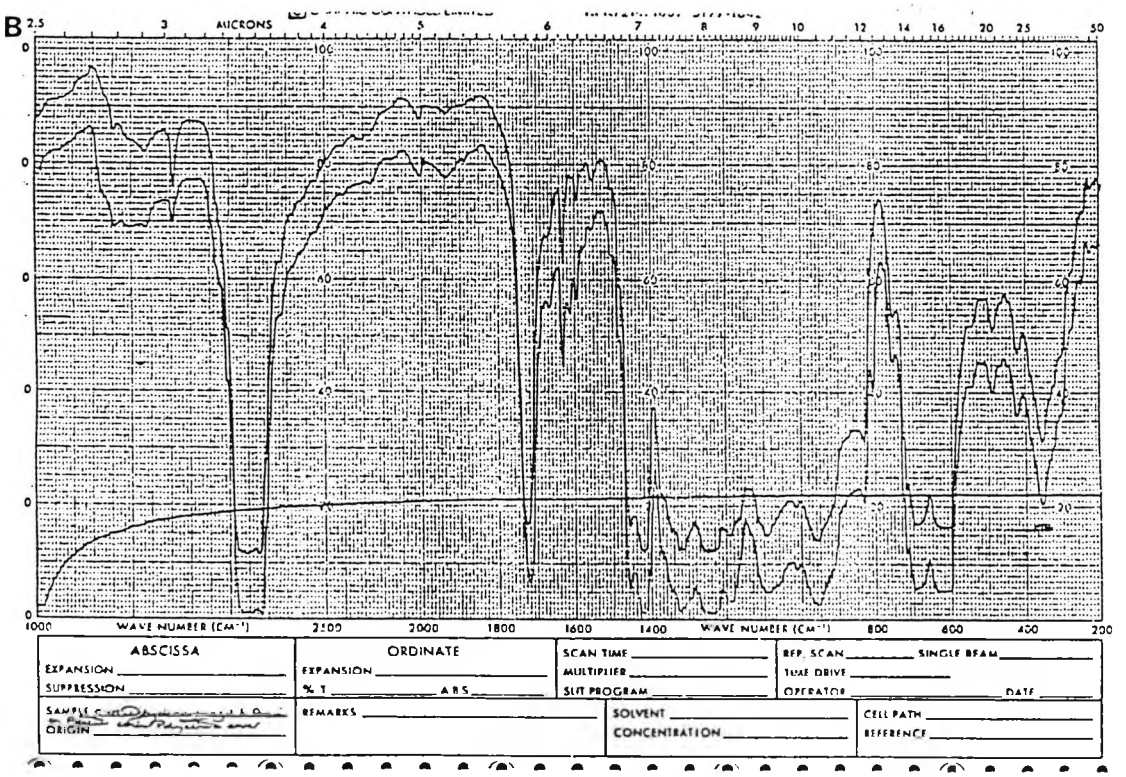
Benzil-4,4'-Diglycidyl Ether





4,4'-Dihydroxybenzil





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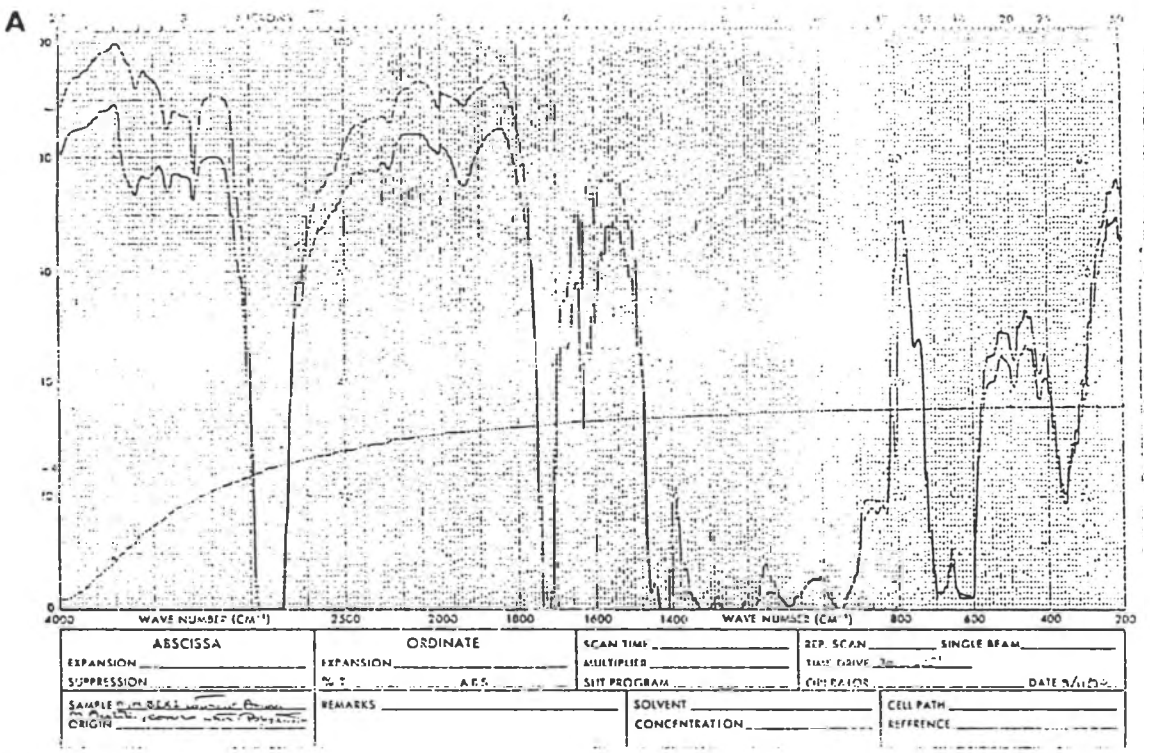
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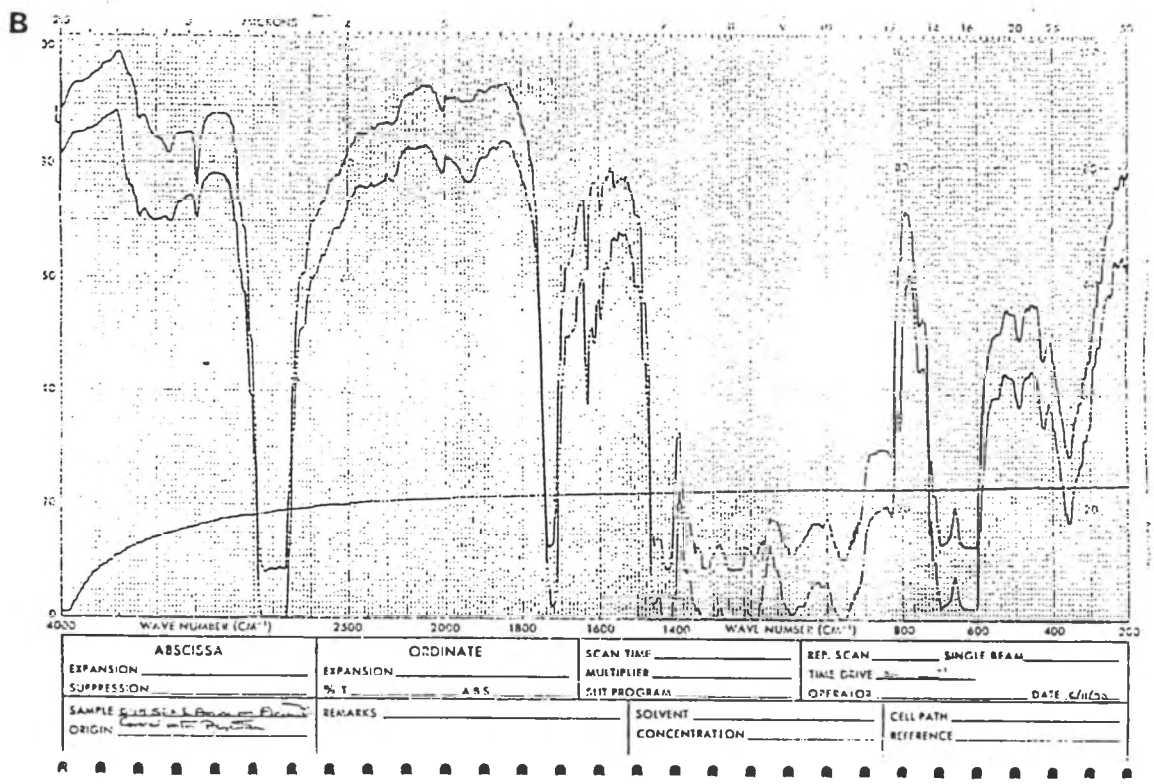
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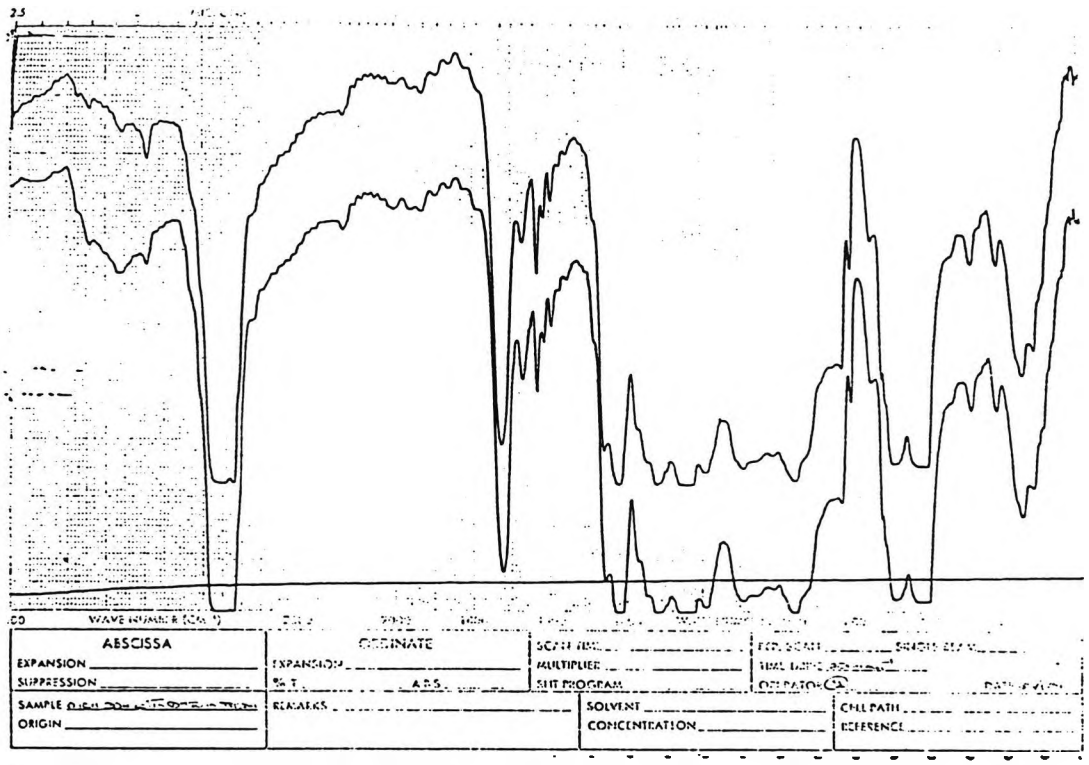
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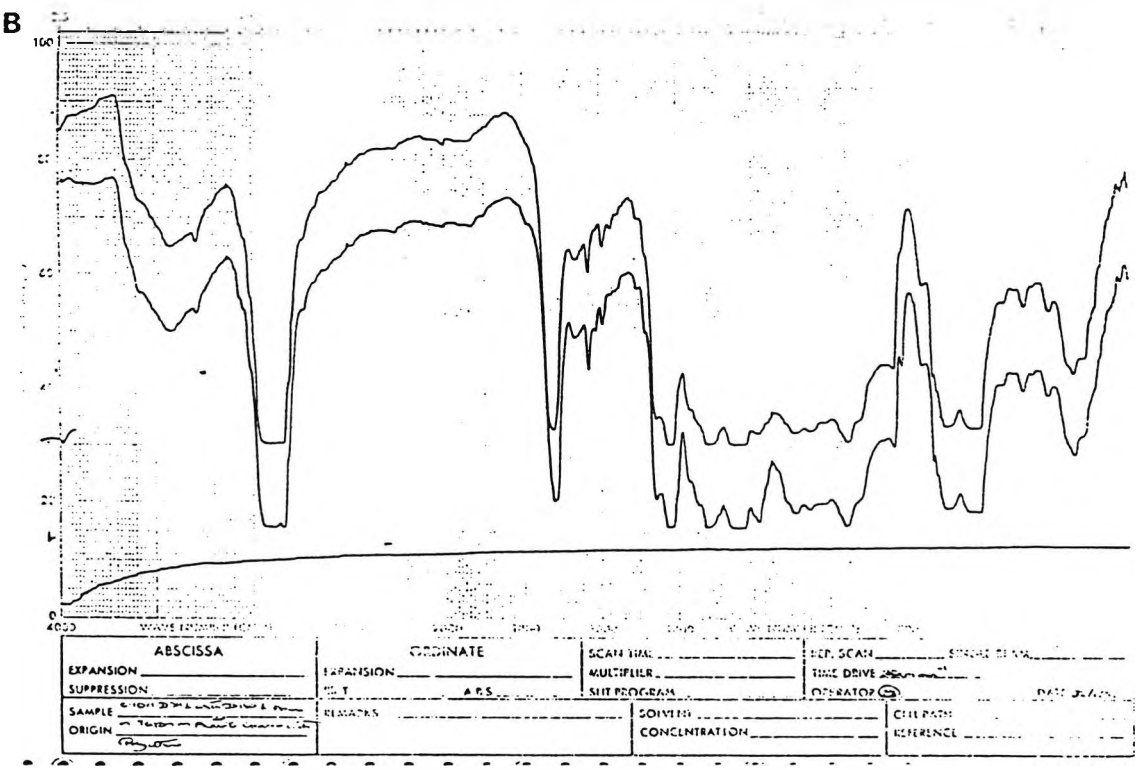
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