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SPECTROSCOPIC PROPERTIES AND PHOTOPOLYMERISATION ACTIVITY OF 4-*n*-PROPOXYTHIOXANTHONE

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Abstract—The influence of various amines on the photoinitiating activity of 4-*n*-propoxythioxanthone in *n*-butyl methacrylate monomer and a commercial triacrylate resin are compared with the spectroscopic and photochemical properties of the initiator in 2-propanol solution. Photopolymerisation activity is highly dependent on the ionisation potential of the amine indicating the involvement of a triplet exciplex with the thioxanthone initiator which undergoes an initial process of electron transfer. Fourier transform i.r. analysis of chloroform extracted cured resin films confirms that the alkylamino radical produced by hydrogen atom abstraction is the species responsible for addition to the acrylate resin and subsequent initiation of the polymerisation and crosslinking reactions. Steady-state photolysis and flash photolysis data confirm the importance of the electron transfer step. The latter study also identifies the absorption spectra of the thioxanthone ketyl radical and radical anion.

INTRODUCTION

Many efforts have been directed toward gaining an understanding of the mechanistic action of photoinitiators under various conditions in order either to develop better and more efficient initiator types or to improve formulations [1–3]. One particular class of photoinitiator consists of the thioxanthones which display high activity when irradiated in the near u.v. with wavelengths up to 400 nm [3]. This feature makes them particularly valuable for the photocuring of white pigmented coatings [4].

Our efforts in this field have involved a deeper understanding of the mode of initiation of thioxanthone initiators as well as developing novel derivatives in order not only to provide further information on the mechanism of initiation but also as a means of improving photoinitiating activity [5–10]. Our results to date indicate two primary mechanisms in initiation of the photopolymerisation of acrylate monomers, both of which involve an intermediate exciplex, they are summarised in Scheme 1, the first involving intramolecular hydrogen atom abstraction from the amine co-synergist to produce a ketyl type radical and an alkylamino radical while the second involves electron abstraction from the amine to give an amine radical cation. The latter then loses a hydrogen atom to give an alkylamino radical.

Scheme 1

T = Thioxanthone; TH. = ketyl radical; T.$^-$radical anion; A = Amine; A.$^-$/A.$^+$ = alkylamino radical/amino radical cation; M = monomer

$$\mathrm{T^* + A \rightarrow [T{-}A]^* \rightarrow [T.^{-}{-}A.^{+}]}$$

Intramolecular hydrogen abstraction

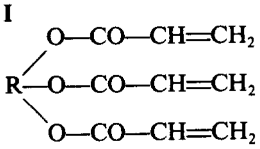
$$\mathrm{A.(\text{–}H) \leftarrow T.^{-} + A.^{+} \qquad A.(\text{–}H) + TH.}$$

$$\mathrm{A.(\text{–}H) + M \rightarrow AM.{-}(\mathit{n}M) \rightarrow AM.\mathit{n} + 1 \rightarrow Polymer}$$

$$\mathrm{TH. + M \rightarrow Polymer}$$

We have established through both spectroscopic and flash photolysis studies that, whilst oil soluble thioxanthones operate primarily through a triplet excited exciplex [5, 7–9], the water soluble types appear to operate through both a singlet and triplet excited complex [6, 10]. The role of the amine in Scheme 1 is clearly an important factor in the initiation step and much of our work indicates that the electron transfer step is important. In this paper we have carried out an in-depth photopolymerisation study on 4-*n*-propoxythioxanthone in the presence of various amines in both a model vinyl monomer (*n*-butyl methacrylate) and a commercial resin (Structure I) and related the data to the spectroscopic properties of the molecule in solution. The results establish a relationship between amine structure and photopolymerisation activity as well as the importance of the electron transfer mechanism in Scheme 1 via an exciplex. Through quantitative steady-state and micro-second flash photolytic studies in the absence and presence of various amines, information is obtained on the nature of the excited state involved as well as the identity of the ketyl and radical anion species. Evidence is also provided, through the use of Fourier Transform i.r. spectroscopy, for addition of the α-alkylamino radical to the acrylate monomer and not the thioxanthone ketyl radical.

I



where R = polyetherpolyol

The 4-*n*-propoxythioxanthone was selected for study since in a recent paper we found that, of all the propoxy derivatives, this molecule exhibited the greatest photoreductive sensitivity in the presence of a tertiary amine [11].

EXPERIMENTAL

Materials

A sample of chromatographically pure 4-*n*-propoxythioxanthone was supplied by Ward-Blenkinsop & Co. Ltd, Widnes, Lancashire, U.K. The melting point and microanalytical data were reported earlier [8]. The triacrylate resin (Structure **I**) was supplied by Lankro Chemicals Ltd, Eccles, Manchester and the tetracyanoethylene, *n*-butyl methacrylate, piperidine, dicyclohexylamine, diethylamine, *N*-methyldiethylamine, triethylamine and tri-*n*-butylamine were obtained from the Aldrich Chemical Co. Ltd. The solvents (chloroform, *n*-butanone and 2-propanol) were all of "Analar" quality and were obtained from Fison's Ltd, U.K.

Spectroscopic measurements

Normal and second-order derivative absorption spectra were obtained using a Perkin–Elmer Model 554 spectrophotometer. Flash photolysis studies were carried out using a conventional micro-second apparatus equipped with two 16 KV xenon filled lamps of 300 J energy output. i.r. Spectra were obtained using a Mattson Fourier-Transform spectrometer (Model Alpha-Centauri).

Photopolymerisation experiments

Rates of photopolymerisation were measured dilatometrically at 30°C utilising a 100 W tungsten/halogen lamp at 10 cm distance. *n*-Butyl methacrylate (50/50 v/v with 2-butanone) was used as the monomer. The initiators and amines were each used at 0.1% w/v concentration.

Photocuring rates, using the triacrylate resin (Structure **I**), were obtained on 12 μm thick coatings on aluminised polyester film irradiated using a 100 W high pressure Hg lamp described earlier [3] and measuring the consumption of the acrylate absorption band at $812\ cm^{-3}$ with respect to the ester band at $1740\ cm^{-1}$ using reflectance i.r. analysis. The latter absorption band operates as an internal standard compensating for shrinkage effects during the curing. A Perkin–Elmer model 1400 i.r. spectrometer was used. Thioxanthone concentrations were 0.5 and 1% w/w whereas the amine concentrations were viable and are quoted in the results.

Steady state photolysis

Solutions (5×10^{-5} M) of the thioxanthone in the absence and presence of various amines (5×10^{-5} M) in argon saturated (< 1 ppm 02) 2-propanol were irradiated using 365 nm monochromatic light isolated from a 200 W high pressure Hg lamp using a Bausch & Lomb monochromator. The light intensity was calibrated using potassium ferrioxalate as the actinometer [12]. Irradiation under polychromatic light was carried out using a Microscal unit utilising a 500 W high pressure Hg/W lamp (Microscal Ltd, London).

RESULTS AND DISCUSSION

Thioxanthone molecules are inefficient photoinitiators when used alone [2]. Their efficiency is very much dependent on the structure of the amine cosynergist. The results in Tables 1 and 2 demonstrate the influence of amines of various ionisation potential on the photopolymerisation of *n*-butyl methacrylate and the triacrylate resin respectively in the presence of 4-propoxythioxanthone. In the former case, polymerisation was monitored volumetrically using dilatometry while in the latter case it was monitored by measured the decrease in the unsaturation absorption at $812\ cm^{-1}$ with respect to the ester band at $1740\ cm^{-1}$ in the i.r. The latter band compensates for changes in film thickness during cure. In both cases it is seen that, with the exception of piperidine, the photoconversion increases with decreasing ionisation potential of the amine. These results confirm our earlier proposal [10] in support of the initial step involving electron transfer via an exciplex shown in Scheme 1. This view is further supported by the results in Tables 3 and 4 which show that the photopolymerisation conversions of *n*-butyl methacrylate and the triacrylate resin increase with increasing concentration of amine (*N*-diethylmethylamine) in the presence of 4-*n*-propoxythioxanthone. Thus, amines with a low ionisation potential induce a higher rate of photopolymerisation. The anomalous behaviour of piperidine may well be due to the inactivity of the ring system for readily abstractable

Table 1. Influence of amines on the conversion of *n*-butyl methacrylate after 60 min irradiation in a dilatometer using 4-*n*-propoxythioxanthone as the photoinitiator (0.1% w/w)

Amine (0.1% w/w)	Ionisation potential	% Conversion (60 min)
Piperidine	9.76	0.192
Dicyclohexylamine	9.20	0.004
Diethylamine	8.40	0.175
N-Diethylmethylamine	8.10	0.304
Triethylamine	7.85	0.583
Tri-*n*-butylamine	7.40	0.658

Table 2. Influence of amines on the conversion of a triacrylate resin after 3 min irradiation using 4-*n*-propoxythioxanthone as the photoinitiator (0.5% w/w)

Amine (0.5% w/w)	Ionisation potential	% Conversion (3 min)
Piperidine	9.76	0.06
Dicyclohexylamine	9.20	0.02
Diethylamine	8.40	0.05
N-Diethylmethylamine	8.10	0.11
Triethylamine	7.85	0.20
Tri-*n*-butylamine	7.40	0.23

Table 3. Influence of *N*-diethylmethylamine concentration on the conversion of *n*-butyl methacrylate after 30 min irradiation using 4-*n*-propoxythioxanthone as the photoinitiator (0.1% w/w)

Amine (% w/w)	% Conversion (30 min)
0.1	0.09
0.2	1.75
0.2	2.12
0.4	2.40

Table 4. Influence of *N*-diethylmethylamine concentration on the percentage conversion of a triacrylate resin after 60 sec irradiation using 4-*n*-propoxythioxanthone as the photoinitiator (1%, w/w)

Amine (% w/w)	% Conversion ($812/1740\,cm^{-1}$) (60 sec)
0	0.07
1	0.22
2	0.30
3	0.35
4	0.45

hydrogen atoms although how this would account for an apparent increase in photopolymerisation activity is uncertain. The activity of the N–H however, may contribute to this effect.

Further confirmation of the importance of the amine in initiating photoplymerisation is demonstrated by the results shown in Fig. 1. In this experiment, thin photocured films of the triacrylate resin (structure I) were refluxed in chloroform for three hours to remove any unbound residual initiator and their spectra recorded using a Fourier Transform i.r. spectrometer. Initiator and amine concentrations were 1% w/w. Control spectra of the uncured resin, thioxanthone and amine (triethylamine) were also recorded. The i.r. spectrum of an extracted-cured film (12 μm thick) is shown in Fig. 1. After comparison with the control spectra, new bands were identified at 1375 cm^{-1} due to the C–N stretch, 1442 cm^{-1} due to vibrational stretching of a combined methylene and methyl group, 848 and 832 cm^{-1} doublet due to a cyclobutane ring and strong doublet band at 762 and 744 cm^{-1} associated specifically with four bonded methylene groups [13]. These bands were not observed in the control spectra apart from the C–N stretch for the amine. The presence of the latter clearly confirms that the alkylamino radical is coupling to the resin whilst the bands at 1442, 762 and 744 cm^{-1} confirm that the active radical is on the B carbon atom of the amine and that this adds directly to the acrylate group thus:

Scheme 2

$$\sim O{-}CO{-}CH{=}CH_2 + \cdot CH_2{-}CH_2{-}N(Et)_2$$
$$\rightarrow \sim O{-}CO{-}C\cdot H{-}CH_2{-}CH_2{-}CH_2{-}N(Et)_2$$

The alkylamino radical may also add to the acrylate double bond at the carbon atom adjacent to the ester group in a similar way. The alkyl radical may then abstract a hydrogen atom from an adjacent acrylate group or another resin molecule.

Although hydrogen atom abstraction is believed to occur primarily from the α-carbon atom in the amine, this is unstable and is believed to revert to the more stable B-position [1, 2]. Our results appear to support this earlier hypothesis. The bands at 848 and 832 cm^{-1} indicates crosslinking across the acrylate groups to give a four membered cyclobutane ring system.

This accelerating effect of the amine on the photopolymerisation activity of thioxanthone initiators is clearly an important factor. The results in Table 5 compare the quantum yields of photoreduction of the thioxanthone initiator in de-oxygenated 2-propanol in the absence and presence of various amines. Such an experiment using monochromatic irradiation allows us to quantify more accurately the acceleration factors involved. The quantum yields of photoreduction range from 0.01 in the absence of an amine to 0.29 in the presence of tri-*n*-butylamine and bear a close similarity to the rates of photopolymerisation in Tables 1 and 2. However, the similar values for triethylamine and tri-*n*-butylamine are difficult to explain. More useful results were obtained under polychromatic irradiation in the Microscal unit and are shown in Fig. 2. Here it is seen that the photolysis

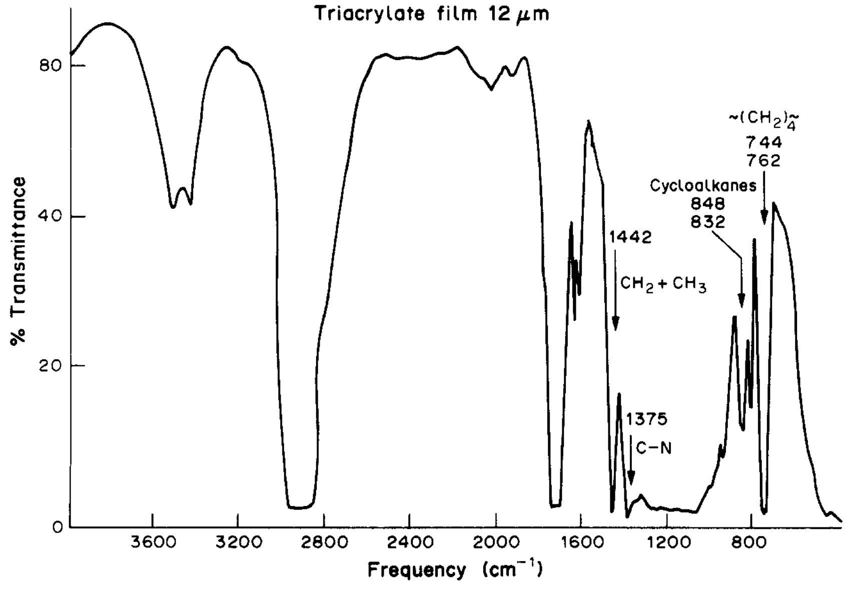


Fig. 1. Fourier transform i.r. spectrum of a chloroform extracted photocured triacrylate film (12 μm thick) with 1% w/w each of 4-*n*-propoxythioxanthone and triethylamine.

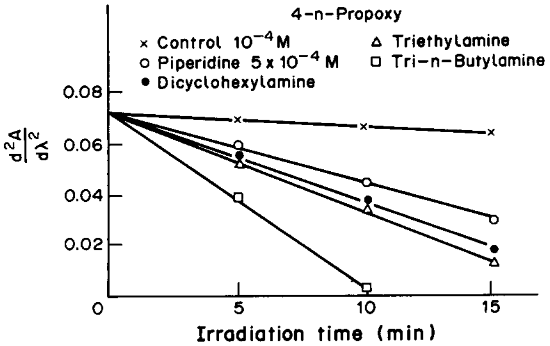


Fig. 2. Rate of photolysis (at 384 nm) using second-order derivative absorption spectroscopy, in the Microscal unit, of 4-*n*-propoxythioxanthone in 2-propanol (10^{-4} M) in the absence (×) and presence of (○) piperidine, (●) dicyclohexylamine, (△) triethylamine and (□) tri-*n*-butylamine (5×10^{-4} M).

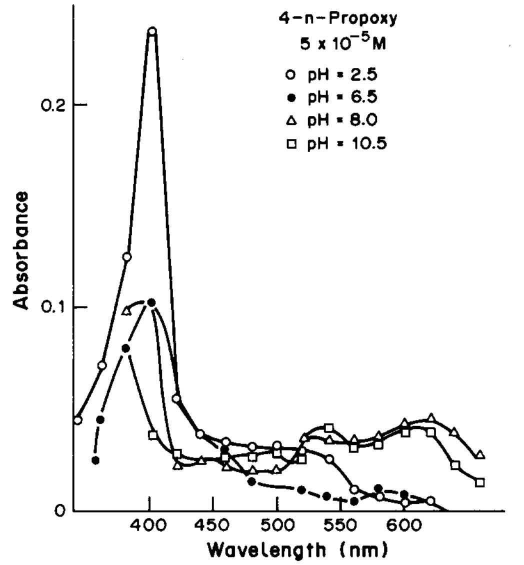


Fig. 3. End-of-pulse transient absorption spectra of 4-*n*-propoxythioxanthone in μ_2 saturated 2-propanol solution (5×10^{-5} M) at a pH of (○) 2.5, (●) 6.5, (△) 8.0 and (□) 10.5

rate of the thioxanthone increases with decreasing ionisation potential of the amine from piperidine to tri-*n*-butylamine. The latter irradiation conditions simulate more closely those used in photopolymerisation. Thus, the steady-state photolysis studies in solution also suggest electron transfer as an important step in the photoreduction mechanism.

End-of-pulse transient absorption spectra of the 4-*n*-propoxythioxanthone were recorded in 2-propanol solution using micro-second kinetic flash photolysis. The effect of pH on transient absorption is shown in Fig. 3. At low pH, strong transient absorption was observed at 400 nm, due to ketyl radical formation, with a weak shoulder between 500–550 nm, due to the radical anion [5–10]. With increasing pH, the absorption profile changes quite dramatically, resulting in a decrease in the ketyl radical absorption followed by an increase in the radical anion absorption together with a red shift toward 600 nm. To distinguish more clearly the identity of the corresponding ketyl radical and radical anion species, transient absorption spectra were recorded in the presence of a hydrogen atom donor viz. benzhydrol (Fig. 4), and also in the presence of increasing concentrations of an amine namely, *N*-diethylmethylamine (Fig. 5). The results in Fig. 4 clearly show that, with increasing the benzhydrol concentration, there is an increase in transient absorption at 380 nm, confirming the identity of the ketyl radical. It should be noted that this experiment was carried out in *n*-hexane to minimise reaction with the solvent. In the absence of a hydrogen donor, no transient was observed. The latter results show that, with increasing amine concentration, there is a marked increase in transient absorption due to both the ketyl radical and the radical anion. The results in Fig. 5 confirm the importance of the radical anion in

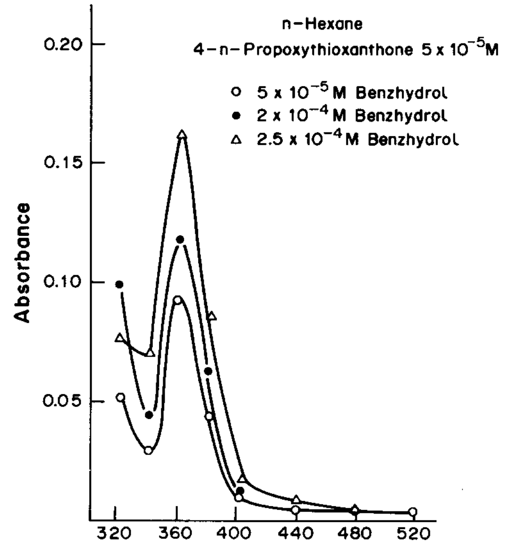


Fig. 4. End-of-pulse transient absorption spectra of 4-*n*-propoxythioxanthone in a μ_2 saturated *n*-hexane solution (5×10^{-5} M) in the presence of (○) 5×10^{-5} M, (●) 2×10^{-4} M and (△) 2.5×10^{-4} M benzhydrol.

Table 5. Quantum yields of photoreduction of 4-*n*-propoxythioxanthone at 365 nm irradiation in argon saturated 2-propanol in the absence and presence of various amines (5×10^{-5} m)

Amine (5×10^{-5} M)	Ionisation potential (eV)	ϕ (Photolysis) 365 nm	Acceleration factor
None	—	0.01	—
Piperidine	9.76	0.04	4.0
Dicyclohexylamine	9.27	0.05	5.0
Triethylamine	7.85	0.29	29.0
Tri-*n*-butylamine	7.40	0.29	29.0

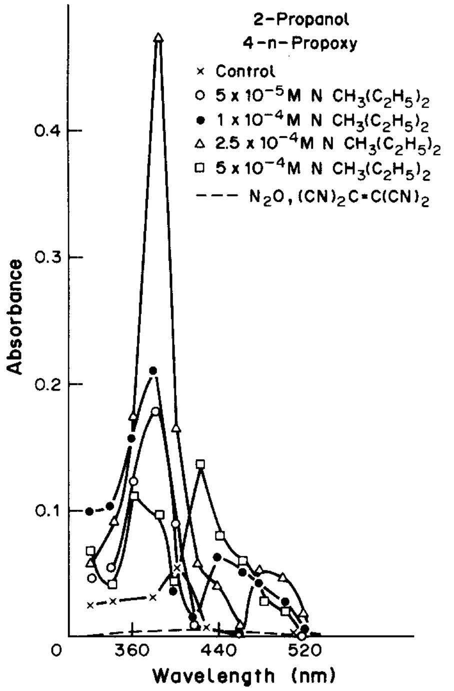


Fig. 5. End-of-pulse transient absorption spectra of 4-*n*-propoxythioxanthone in μ_2 saturated 2-propanol solution in the (×) absence and presence of *N*-diethylmethylamine at (○) 5×10^{-5} M, (●) 1×10^{-4} M, (△) 2.5×10^{-4} M and (□) 5×10^{-4} M. (-----) Transient absorption spectrum in the presence of tetracyanoethylene (10^{-4} M) and after saturation with nitrous oxide gas.

transient production where it is seen that saturation of the solution with nitrous oxide, an electron trap, completely quenches transient formation. The latter result is further supported by the observation that the addition of tetracyanoethylene, another well-known electron trap also quenches transient formation. In our earlier work on water soluble thioxanthones [10], only partial quenching of the radical anion absorption was observed on saturation of water solutions of the initiator with nitrous oxide. This we believe was probably due to the poor solubility of the latter in water.

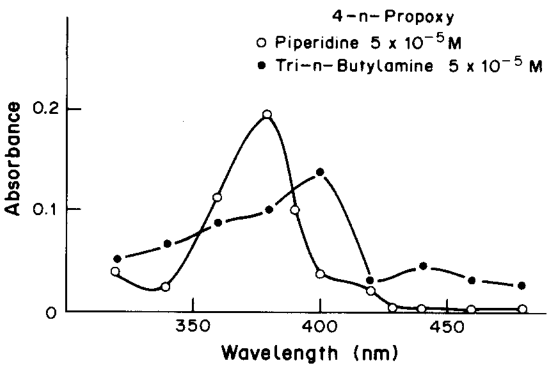


Fig. 6. End-of-pulse transient absorption spectra of 4-*n*-propoxythioxanthone in μ_2 saturated 2-propanol in the presence of (○) piperidine and (●) tri-*n*-butylamine (5×10^{-5} M).

The effect of different amines on transient absorption spectra are compared in Table 6. An exact correlation between transient absorption due to the ketyl radical/radical anion and the ionisation potential of the amine is difficult due to various structural differences in the amines although there is a trend. For example, Fig. 6 compares the transient absorption spectra for 4-*n*-propoxythioxanthone in the presence of two amines, viz. piperidine and tri-*n*-butylamine, where it could be argued that there is a red shift in the transient absorption spectrum with decreasing ionisation potential of the amine. Finally, as found earlier all the transient absorptions were strongly quenched in the presence of oxygen indicating the involvement of the lowest excited triplet state in radical formation.

CONCLUSIONS

These results provide evidence in support of a mechanism involving a triplet exciplex in the photopolymerisation of acrylate monomers and resins by oil soluble thioxanthone initiators with an amine co-synergist. Electron abstraction is the primary mechanism of photoreduction followed by hydrogen abstraction from the amine to give an alkylamino radical. The latter then adds on to the acrylate group initiating polymerisation.

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Table 6. Influence of amines on the end-of-pulse transient absorption maxima for 4-*n*-propoxythioxanthone in 2-propanol (5×10^{-5} M)

		Absorbance			
		Radical		Radical anion	
Amine	Ionisation potential	nm	ABS	nm	ABS
None	—	NO		400	0.055
Piperidine	9.76	380	0.22	400(s)	0.040
Dicyclohexylamine	9.20	360	0.28	420	0.070
Diethylamine	8.40	380	0.12	420	0.040
				480	0.030
N-diethylmethylamine	8.10	380	0.30	440	0.035
Triethylamine	7.85	340(s)	0.075	400	0.075
				480	0.030
Tri-*n*-butylamine	7.40	360(s)	0.075	400	0.130
				440	0.045
Diphenylamine	7.40	380	0.16	420	0.110
				480(s)	0.020

(s) = Shoulder.
NO = Not observed.

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