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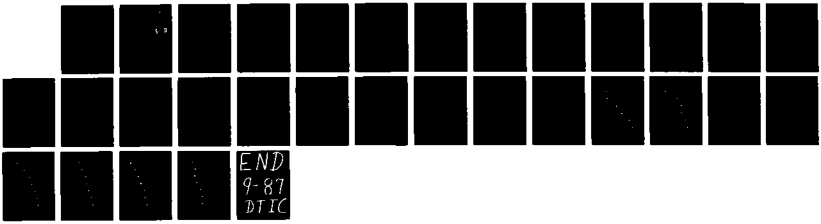

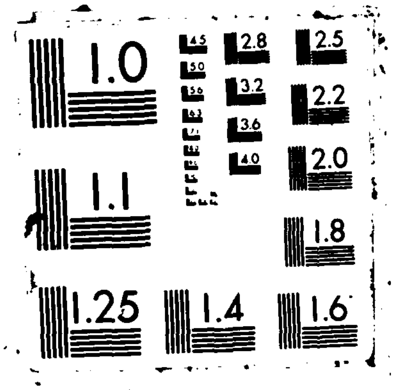
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THE EFFECT OF FLEXIBILITY ON THE PHOTODEGRADATION OF AROMATIC DIISOCYANATE BASED POLYURETHANES

by

Charles E. Hoyle and Kyu-Jun Kim

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Department of Polymer Science
University of Southern Mississippi
Southern Station Box 10076
Hattiesburg, MS 39406-0076

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The photolytic degradation of 2,4-TDI/aliphatic diol polyurethanes is directly dependent on the flexibility of the polymer backbone. The extent of photodegradation is accelerated above the glass transition temperature indicating the role of chain flexibility and/or oxygen diffusion in the decomposition process. Photolysis of the model compound ethyl N-phenylcarbamate (EPC) in neutral host polymer matrices indicates that the para photo-Fries to ortho photo-Fries product ratio experiences an accelerated increase with temperature above the glass transition of the polymer matrix.

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Abstract

The photolytic degradation of 2,4-TDI/aliphatic diol polyurethanes is directly dependent on the flexibility of the polymer backbone. The extent of photodegradation is accelerated above the glass transition temperature indicating the role of chain flexibility and/or oxygen diffusion in the decomposition process. Photolysis of the model compound ethyl N-phenylcarbamate (EPC) in neutral host polymer matrices indicates that the para photo-Fries to ortho photo-Fries product ratio experiences an accelerated increase with temperature above the glass transition of the polymer matrix.

(Keywords: photodegradation; toluene diisocyanate; polyurethane; flexibility effect; photo-Fries rearrangement; glass transition temperature)

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INTRODUCTION

Polyurethanes based on aromatic diisocyanates are quite useful in a number of industrial applications ranging from processed foams to certain coatings applications. However, in instances where exposure to UV radiation from sun light is required, they are found to rapidly degrade with loss of physical integrity and discoloration[1-3]. One of the most popular aromatic diisocyanates used to make polyurethanes is based on toluene diisocyanate (TDI) and actually consists of a particular mixture of 2,4-TDI and 2,6-TDI isomers. In order to provide a basis for interpretation of the data presented in this paper, a brief literature review of the polyurethane photolysis literature is presented with emphasis on polymers based on TDI.

In a series of studies, Schollenberger and coworkers [7-10] proposed that the photolysis of 2,4-TDI based polyurethanes resulted in the formation of quinoid type structures (See references 7-10 for schemes and discussions). In other investigations, based primarily on the results obtained for photolysis of model compounds, Beachell and Chang[11] postulated that TDI based polyurethanes decomposed at least in part by a photo-Fries rearrangement process upon photolysis. Subsequent studies have verified the validity of this premise[12-14]. Despite the number of reports on the photolysis of aromatic polyurethanes, none of the studies to date have considered the effect of polymer chain flexibility upon the photodegradation of TDI based polyurethanes. This paper serves to address this issue by presenting results for the photolysis of a series of 2,4-TDI based polyurethanes. By comparison of the photolytic decomposition of a series of amorphous 2,4-TDI/aliphatic diol polyurethanes with increasing chain flexibility, the effect of chain stiffness on the polymer decomposition is elucidated. By utilizing model compounds in restrictive polymer matrices, i. e., polymethylmethacrylate (PMMA), polyethylmethacrylate (PEMA), and polybutylmethacrylate (PBMA), it is confirmed that polymer chain/matrix flexibility can be a contributing factor to the initial photo-Fries product distribution.

EXPERIMENTAL SECTION

Materials 2,4-TDI (99.5%) was obtained from Mobay and distilled before polymerization. All diols were purchased from Aldrich. 1,2-Ethylene glycol, 1,4-butanediol, and 1,6-hexanediol were purified by vacuum distillation. 1,8-Octanediol, 1,10-decanediol, and 1,12-dodecanediol were recrystallized from 1,2-dichloroethane. Polyurethanes were synthesized by a solution polymerization[15]. A typical example is given. To a solution of 2,4-TDI (4.5g,

2.58×10^{-2}mol) in 10ml of DMSO (distilled and dried), 1,8-octanediol (3.8g, 2.58×10^{-2} mol) in 10 ml of DMSO was added dropwise with stirring through an addition funnel under a nitrogen stream. The reaction mixture was heated up to 115°C. After stirring for 2 hours, the resulting viscous mixture was diluted with 20ml of dimethylformamide (DMF) and poured dropwise into 1000 ml of deionized water to precipitate the polymer. The isolated polymer (designated TDI-8) was washed with fresh water and dried in a vacuum oven. The intrinsic viscosities of the polyurethanes synthesized by this procedure were 0.20dl/g (TDI-2), 0.20dl/g (TDI-4), 0.15dl/g (TDI-6), 0.18dl/g (TDI-8), 0.16dl/g (TDI-10), and 0.14dl/g (TDI-12) in DMF at 25 °C. Ethyl N-phenylcarbamate(EPC) was prepared from phenyl isocyanate and ethanol in ethyl acetate. Ethyl 2-amino benzoate, ethyl 4-amino benzoate, and aniline were obtained from Aldrich. PMMA (Aldrich), PEMA (Polysciences), and PBMA (Aldrich) were purified by multiple precipitations in cyclohexane. The molecular weights calculated from the intrinsic viscosities were 1.27×10^5 (PMMA, acetone at 25 °C), 2.96×10^5 (PEMA, ethyl acetate at 35 °C), and 2.81×10^5 (PBMA, acetone at 25 °C).

Instrumentation/Procedure A 100 Watt medium pressure mercury lamp was used without any filter for the results in Figures 2 and 3. For the rest of the photolyses, a 450 Watt medium pressure Hanovia mercury lamp was used with an appropriate filter (Pomfret Research Optics 280nm line filter or Corning 7-54 band filter, transmitting wavelength 240nm-400nm). A small fan was employed to cool the lamp source. The polyurethane films were cast from DMF solutions in aluminum pans for the gel formation studies and on quartz plates for the UV absorption measurements. The photolysis temperature was controlled with a home-built cell. A heating pad was placed inside the aluminum box and controlled by a powerstat plugged into the output of a solid state relay system. A quartz window (5cm x 5cm) was clamped by a spring on the front side of an aluminum box and the sample was inserted between the quartz window and the surface of the aluminum plate. A thin film resistence thermometer probe (Omega) was affixed on the front side of the aluminum box and connected to a solid state relay (Omega) to monitor and control the surface temperature. For model compound photolysis, films were cast on the quartz disc (1.5" diameter) from solution (1 ml) containing 0.5g of the polymer matrix, 0.025g EPC, and 20 ml dichloroethane. The cast films were dried for 8 hours in the dark at a room temperature and then irradiated for 4 hours (Mercury lamp with 280 nm line filter). The photolyzed samples (in each case three samples were combined together to provide enough material for HPLC evaluation) were separated from the quartz disc by immersing in water followed by soaking in methanol (3 ml). The separation of the small molecule products from the polymer matrix was accomplished by soaking in methanol for 2 days in a refrigerator. The photoproducts in methanol were analyzed by HPLC. μ-Bondapak CN and μ-bondapak C_{18} columns were connected in a series and CH_3CN/water (50/50 vol. %) was used as the mobile phase. The retention times were 14.0 min (EPC), 11.5 min (aniline), 12.6 min (ethyl 4-amino benzoate), 16.2 min (ethyl 2-amino benzoate), and 23.6 min (naphthalene, internal standard) at a 0.7 ml/min flow rate. The wavelength of the detector (Waters Model 481 LC Spectrophotometer) was 300nm for the para photo-Fries product analysis and 315nm for the ortho photo-Fries product analysis. UV absorption as measured on a Perkin-Elmer 320 UV spectrophotometer and the thermal transition as recorded on a Dupont 910 DSC at a 3 °C/min heating rate.

RESULTS AND DISCUSSION

The results of our investigation will be presented in two parts. The first part deals with the effect of polymer chain flexibility on the photodegradation of polyurethanes based on 2,4-TDI and aliphatic diols. The second part pertains to the effect of polymer matrix flexibility on the photo-Fries rearrangement process of a small molecule aryl carbamate. The aryl carbamate is used as a model for the carbamate moiety in the backbone of the aromatic polyurethanes.

Flexibility Effect It is well known that 2,4-TDI based polyurethanes, due to the asymmetrical structure of the parent diisocyanate, are amorphous. This provides an excellent opportunity to investigate the effect of polymer chain flexibility on the photodegradation process. Accordingly, by reacting 2,4-TDI with diols of increasing methylene segments, a homologous series of polymers is produced with increasing numbers of methylene groups in the aliphatic portion of the chain. A list of six polymers synthesized for this study is given in Table I. The polymers are named according to the number of methylene chain segments in the parent diol used to make the polymer. DSC traces shown in Figure 1 provide the glass transition temperatures (T_g) of the polymers listed in Table I. Each polymer was cast from a DMF solution (0.5g/dl) to give a film approximately 20 μ thick. The absorption spectra of TDI based polyurethanes and model aryl carbamates is well documented in the literature[1,11,16]. A recently published spectrum[16] of ethyl N-phenylcarbamate is characterized by an absorbance maximum at 274nm (ϵ ~1000), falling off to zero by 300nm. Thus, photolysis is readily accomplished with 254nm, 267nm, or 280nm lines of a medium pressure mercury lamp source. Photolysis of the films with a 100 Watt Mercury lamp (12 hr, 25°C) was followed by recording the change in UV absorption at 400nm and the percent gel formation. Both measurements have been employed extensively in the past to indicate the extent of photodegradation of polyurethanes[8]. The plots in Figures 2 and 3 indicate that photolysis of the polyurethanes with higher chain flexibility, i. e., those with low T_g's, results in higher yields of crosslinked gel and UV absorbance changes. This is not totally unexpected. Earlier studies in this series[16,17], as well as those of others[11,14], have postulated that the photo-Fries rearrangement process and subsequent photooxidation of the arylamine products is at least one of the mechanisms for the photolytic degradation of 2,4-TDI based polyurethanes. It can be speculated that the matrix flexibility may control the overall generation of colored products and formation of a highly crosslinked matrix. Evidence for photo-Fries product formation in the photolysis of 2,4-TDI based polyurethanes has recently been provided by a detailed fluorescence analysis[16]. It should be noted that the initial photo-Fries product formation is insensitive to oxygen[19]. However, it is well documented that the aromatic amines resulting from the photo-Fries rearrangement process are themselves readily converted in the presence of oxygen to highly colored azo compounds[11]. This is confirmed by the relatively rapid buildup in the absorbance at 400nm of 2,4-TDI based polyurethanes in the presence of oxygen (as opposed to photolysis in an inert atmosphere). As a result, the increase in absorbance at 400nm and percent gel formation with increasing length of the methylene chain in the parent diol may well be due to flexibility effects on initial photo-Fries product formation, large-scale segmental mobility required for gel formation, and an increased rate of oxygen diffusion in the more flexible films. The effect that flexibility plays in the initial efficiency of photo-Fries product formation and product distribution is demonstrated in the next section for a model carbamate in a series of rigid polymer matrices.

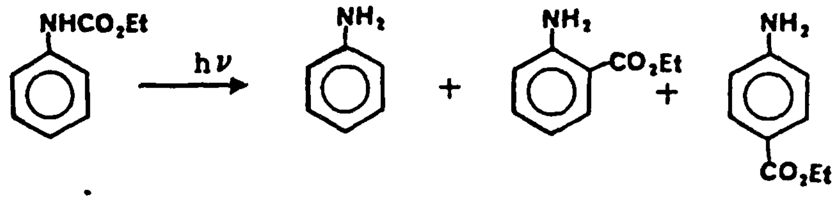
Having shown the effect of chain flexibility on the photolytic degradation of 2,4-TDI based polyurethanes, three of the polyurethanes listed in Table I (TDI-2, TDI-6, and TDI-10) were chosen for further temperature studies. Each of the films was photolyzed at a series of temperatures [Mercury lamp, Corning 7-54 filter, 1 hour]. A plot of the absorbance at 400nm versus photolysis temperature for each of the photolyzed films is shown in Figure 4. In all three cases there is a rather modest increase in absorbance at lower temperatures followed by a rapid increase above a certain critical temperature (T_{cr})(Table I). This critical temperature depends on the polymer backbone structure, decreasing with an increase in polymer chain flexibility. Similiar results are shown in Figure 5 for the increase in gel formation with photolysis temperature (Mercury lamp, Corning 7-54 filter, 3 hours). The critical temperatures for the the onset of increase in gel formation (obtained from Figure 5) are also listed in Table I. The critical temperatures obtained from Figures 4 and 5 can be compared with the

T_g's for these polymers measured by DSC (Table I). Obviously the critical temperatures coincide with the T_g's. One can conclude that above the T_g there is a significant increase in the extent of photodegradation for TDI-2, TDI-6, and TDI-10. These results are consistent with the well recognized change in the coefficient of expansion of polymer systems at T_g. The change in the coefficient of expansion is directly related to co-operative long-chain segmental motion in the polymer backbone, which causes a constant and significant increase in free volume above T_g. One readily envisions that above T_g the processes leading to the crosslinking and colored product formation are enhanced by the increase in free volume and long range segmental mobility as discussed previously.

Photolysis of Ethyl N-Phenylcarbamate in Inert Polymer Matrices In order to provide basic information about the flexibility effect on the initial photo-Fries product formation of polyurethanes based on 2,4-TDI which have arylcarbamate chromophores in the backbone, a model small molecule ethyl N-phenylcarbamate (EPC) was chosen for photolysis studies. The photo-Fries mechanism for this model system has been thoroughly analyzed by a number of groups[18-23]. The three major products formed on photolysis of EPC (1) in either solution or a solid matrix are shown in Scheme I.

Our attention will be directed toward the formation of the ortho photo-Fries (3) and para photo-Fries (4) products in PMMA, PEMA, and PBMA. The yield of aniline (2) is rather low in these polymer matrices and can not be easily quantified.

Scheme I



1 2 3 4

EPC was incorporated into the three host polymer matrices at low percentages (5 % by weight). Quantification of photoproduct formation was accomplished by direct analysis of photolyzed samples using HPLC to separate products 3 and 4. By soaking each of the photolyzed films containing EPC in methanol (a non-solvent for the host polymer matrices) the products produced during photolysis, along with the starting EPC, can be readily recovered in quantitative yield. A check of the UV spectra of the host matrix films (PMMA, PEMA, and PBMA) after the 2 day soaking process indicates that the photoproducts and starting material have been efficiently removed. The HPLC analysis was made by comparison of the peak area of photoproducts 3 and 4 with authentic samples independently prepared.

Results for photolysis of EPC (2.27×10^{-5}mol) in PMMA and PEMA matrices (film thickness ~ 20 μ) are given in Figures 6 and 7 for photolysis at temperatures ranging from 30 °C to 90 °C (All films were photolyzed for 4 hours with the isolated 280nm output of a medium pressure mercury lamp system. The absorbance of the EPC was about 0.4). Figures 6 and 7 show that both para photo-Fries (4) and ortho photo-Fries (3) product formation is non-linear with temperature. The non-linearity is particularly noticeable for para photo-Fries product formation. Figure 8 shows a plot of the ratio of the para to ortho photo-Fries product as a function of photolysis temperature. In each case, there is a change in the slope at a transition temperature (T_{tr}) which is dependent on the particular matrix, i. e., 49 ± 5 ^{o}C for PEMA and 70 ± 5 ^{o}C for PMMA. In order to provide a basis for interpreting the results in Figure 8, DSC scans were recorded tor PEMA and PMMA films filled with 5% EPC. In Table II, results of the glass transition temperatures obtained from the DSC scans as well as the transition temperatures from Figure 8 are compiled. It is readily seen that the transition temperatures (T_{tr}) from Figure 8 are essentially the same as the glass transition temperatures obtained from the DSC. Apparently, the increase in flexibility in the host PEMA and PMMA matrices which occurs at T_g favors the para photo-Fries product. This stems from the requirement that for the para photo-Fries product to form significant radical movement for recombination must occur. The ortho photo-Fries product does not demand the same degree of radical movement.

In order to provide corroborative evidence for the observations in PMMA and PEMA, the photolysis of EPC as conducted in PBMA which has a T_g of 30 ^{o}C (Table II). The ratio of the para to ortho photo-Fries product upon photolysis increases linearly with temperature from 30 ^{o}C to 90 ^{o}C (Figure 9). Since the T_g for the PBMA film with 5% EPC is 30 ^{o}C, no change in slope of the para to ortho photo-Fries product occurs at the temperatures employed.

An interesting comparison can be made between photolysis of EPC in PEMA and PBMA versus EPC in PMMA films at the highest temperature employed (90 ^{o}C) in this investigation. For PEMA and PBMA at 90 ^{o}C the ratio of the para to ortho photo-Fries product is slightly greater than 1.0. For the much stiffer PMMA matrix the ratio is only about 0.6 at 90 °C. At 90 °C, both PEMA and PBMA are well above their glass transition temperatures. This apparently provides a mechanism for the para photo-Fries recombination process to compete more favorably with the ortho photo-Fries process. However, at 90 °C PMMA is only slightly above its glass transition temperature. Consequently, formation of the para photo-Fries product relative to the ortho photo-Fries product is retarded.

In summary, the host polymer matrix has a definite measurable effect on the para to ortho photo Fries product ratio for a model aryl carbamate. In the more flexible matrices, the para photo-Fries product is enhanced. However, changes in absolute yield of either the para or ortho photo-Fries product above the T_g of the host matrix are not dramatic. In contrast to the photo-Fries product formation in the model systems, the polyurethane photodegradation results for gel formation and absorbance changes show a dramatic increase above the polymer T_g. Of course in the polyurethane case the radicals generated in the primary N-C bond cleavage are part of the polymer backbone. But perhaps of more importance is the fact that the photoreactions leading to crosslinking and absorbance increases, which occur following the photo-Fries rearrangement process, are heavily dependent on both large-scale segmental motion by adjacent chains and oxygen diffusion. It is this dependence which may well account for the abrupt effect noted at T_g for the 2,4-TDI based polyurethanes.

CONCLUSION

By combining two sets of studies, one on a series of 2,4-TDI based polyurethanes with varying flexibility and the second on the photo-Fries rearrangement of a small molecule model compound in polymer host matrices, the effect of matrix flexibility on the photolysis of aromatic diisocyanate based polyurethanes has been clearly demonstrated. In the case of the 2,4-TDI/aliphatic diol polyurethanes, the extent of photodegradation, as measured by the increase in UV absorbance and gel formation, is dependent on the length of the aliphatic portion ,and consequently the flexibility, of the polymer.

In general, this study indicates the necessity of taking into account the flexibility of polyurethanes on their photodegradation process. It is not sufficient to assume that because polymers share a common photoreactive backbone group they will degrade by either the same mechanism or to the same extent. This theme will be amplified in future publications presently in progress.

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Table I. T_g and T_{cr} for TDI Based Polyurethanes

Polymer	T_g[a] (°C)	T_{cr}[b] (°C)	T_{cr}[c] (°C)
TDI-2	70	70	70
TDI-4	65	--	--
TDI-6	62	60	60
TDI-8	52	--	--
TDI-10	43	42	40
TDI-12	31	--	--

[a] Obtained from midpoint of glass transition by DSC.

[b] Obtained from Figure 4.

[c] Obtained from Figure 5.

Table II. T_g and T_{tr} for EPC Photolysis in Host Polymer Matrices.

Polymer Host Matrix	T_{tr}[a] (°C)	T_g[b] (°C)
PMMA	75 ± 5	80 ± 5
PEMA	55 ± 5	55 ± 5
PBMA	----	30 ± 5

[a] Obtained from midpoint of glass transition by DSC.

[b] Obtained from Figure 8.

Figure Captions

Figure 1. DSC scans for a series of aliphatic diol polyurethanes.

Figure 2. Absorbance increase at 400nm for a series of 2,4-TDI/aliphatic diol polyurethanes with increasing number of methylene chain segments.

Figure 3. Gel percent increase upon photolysis for a series of 2,4-TDI/aliphatic diol polyurethanes with increasing number of methylene chain segments.

Figure 4. Absorbance increase at 400nm for (a) TDI-2, (b) TDI-6 and (c) TDI-10 as a function of photolysis temperature.

Figure 5. Gel percent increase for (a) TDI-2, (b)TDI-6, and (c) TDI-10 as a function of photolysis temperature.

Figure 6. Formation of para photo-Fries product (4) as a function of photolysis temperature in PEMA (●) and PMMA (○) host matrices.

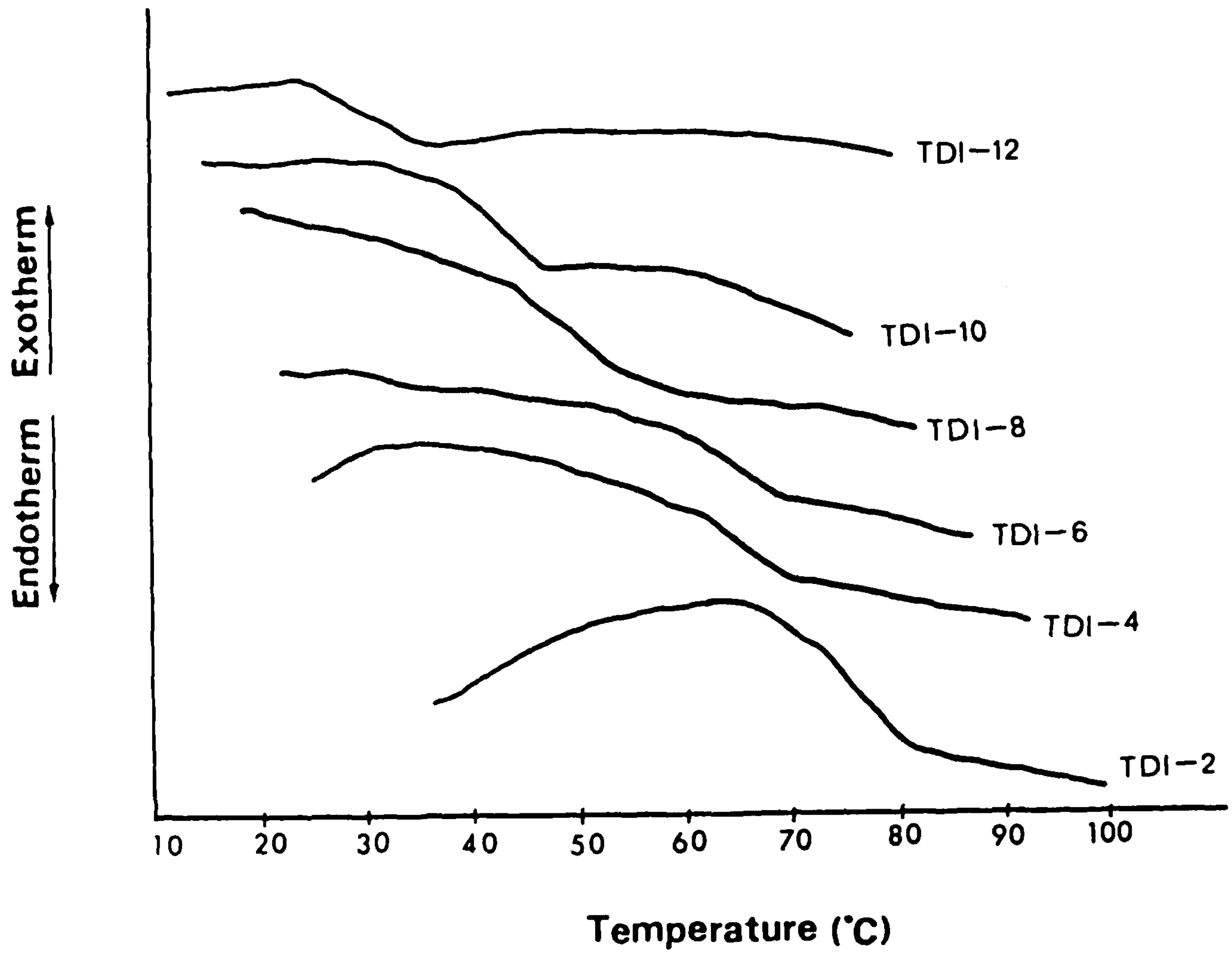
Figure 7. Formation of ortho photo-Fries product (3) as a function of photolysis temperature in PEMA (●) and PMMA (○) host matrices.

Figure 8. Ratio of para (4) to ortho (3) photo-Fries products as a function of photolysis temperature in PEMA (●) and PMMA

(○) host matrices.

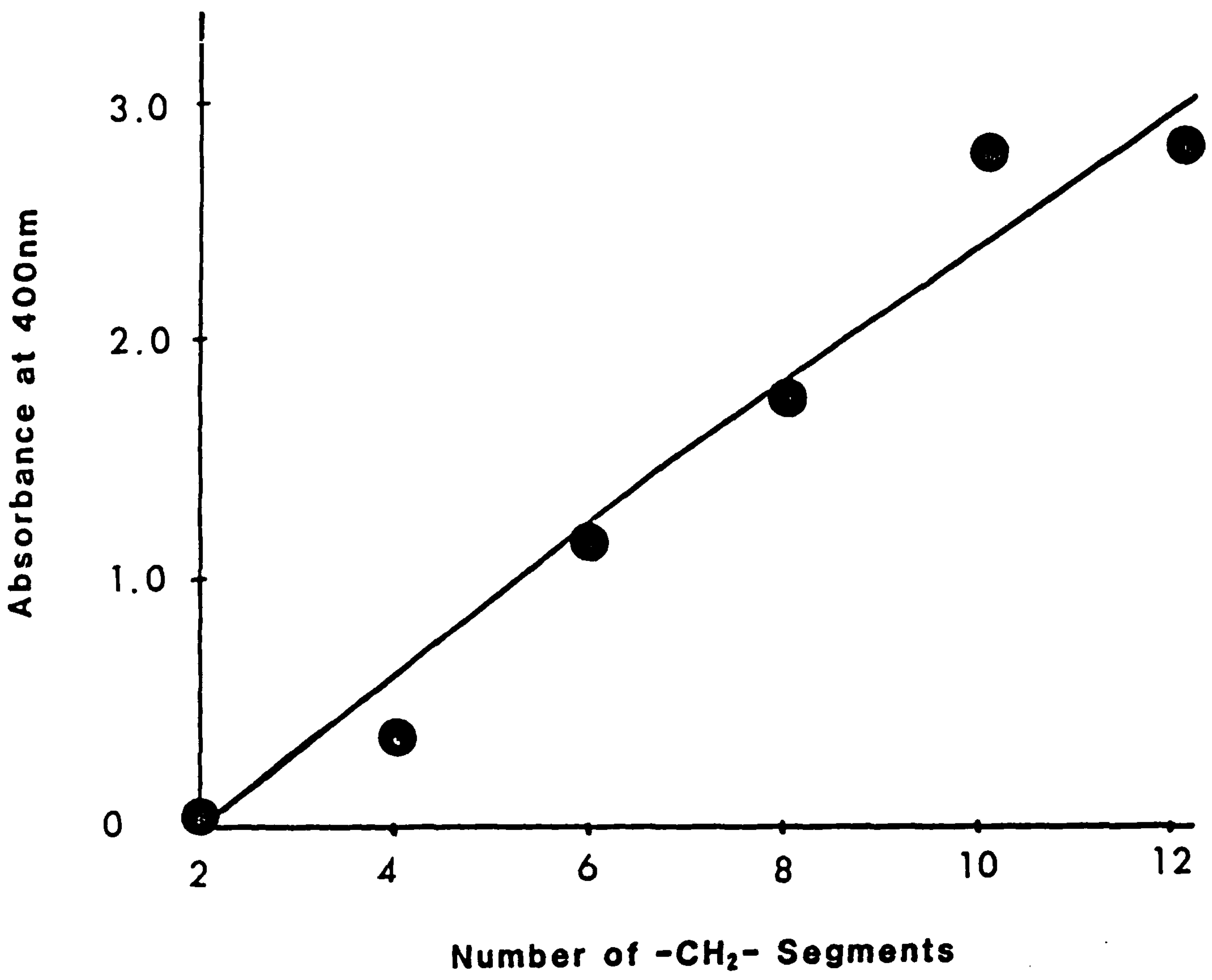
Figure 9. Ratio of para (4) to ortho (3) photo-Fries products as a function of photolysis temperature in PBMA host matrix.

Fig 1.



Exotherm
Endotherm
TDI−12
TDI−10
TDI−8
TDI−6
TDI−4
TDI−2
10
20
30
40
50
60
70
80
90
100
Temperature (°C)

Fig. 2


Absorbance at 400nm
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2.0
1.0
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2
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6
8
10
12
Number of -CH₂- Segments

Fig. 3

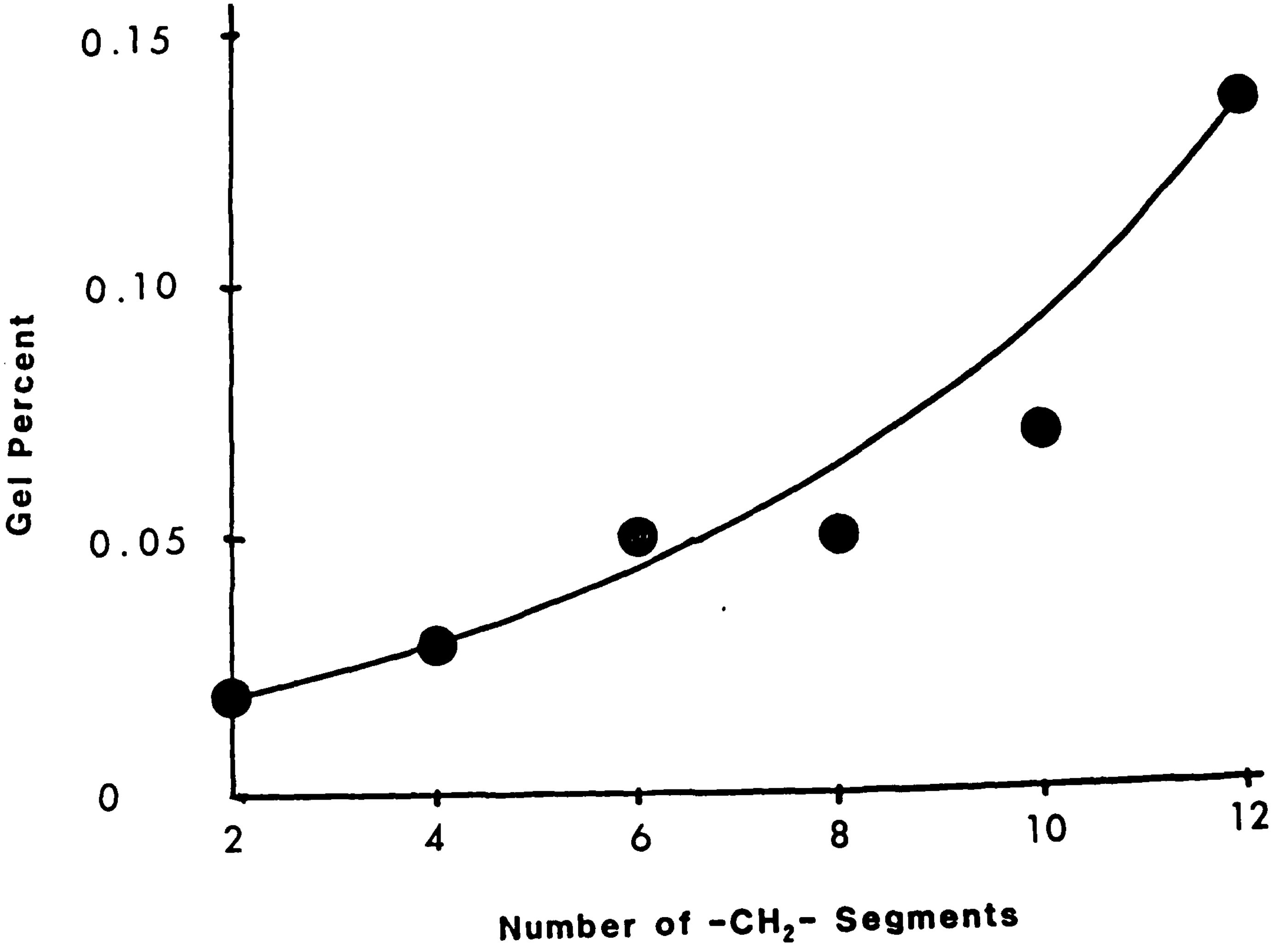
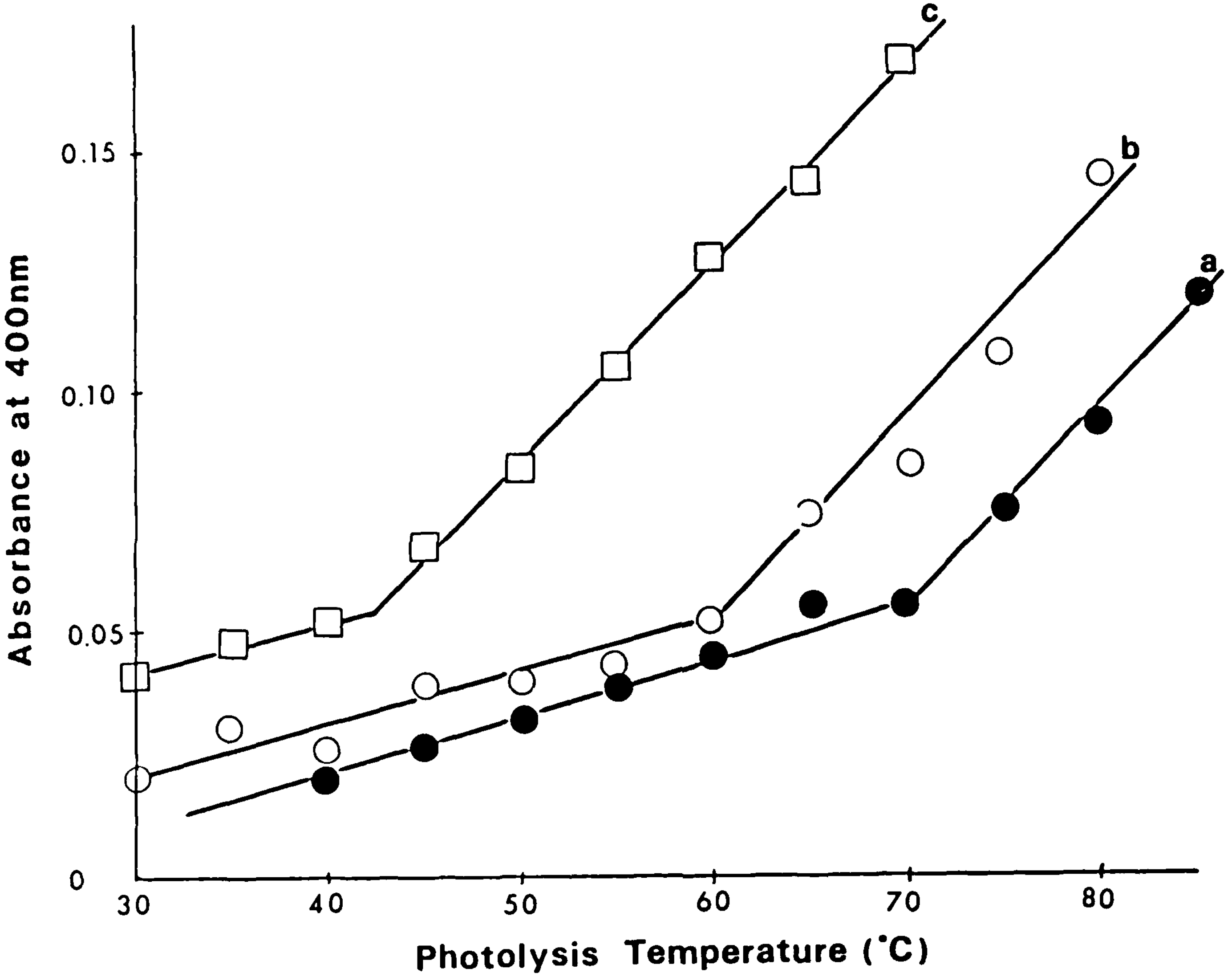


Fig 9



c
b
a
0.15
0.10
0.05
0
Absorbance at 400nm
30
40
50
60
70
80
Photolysis Temperature (°C)

Fig 5

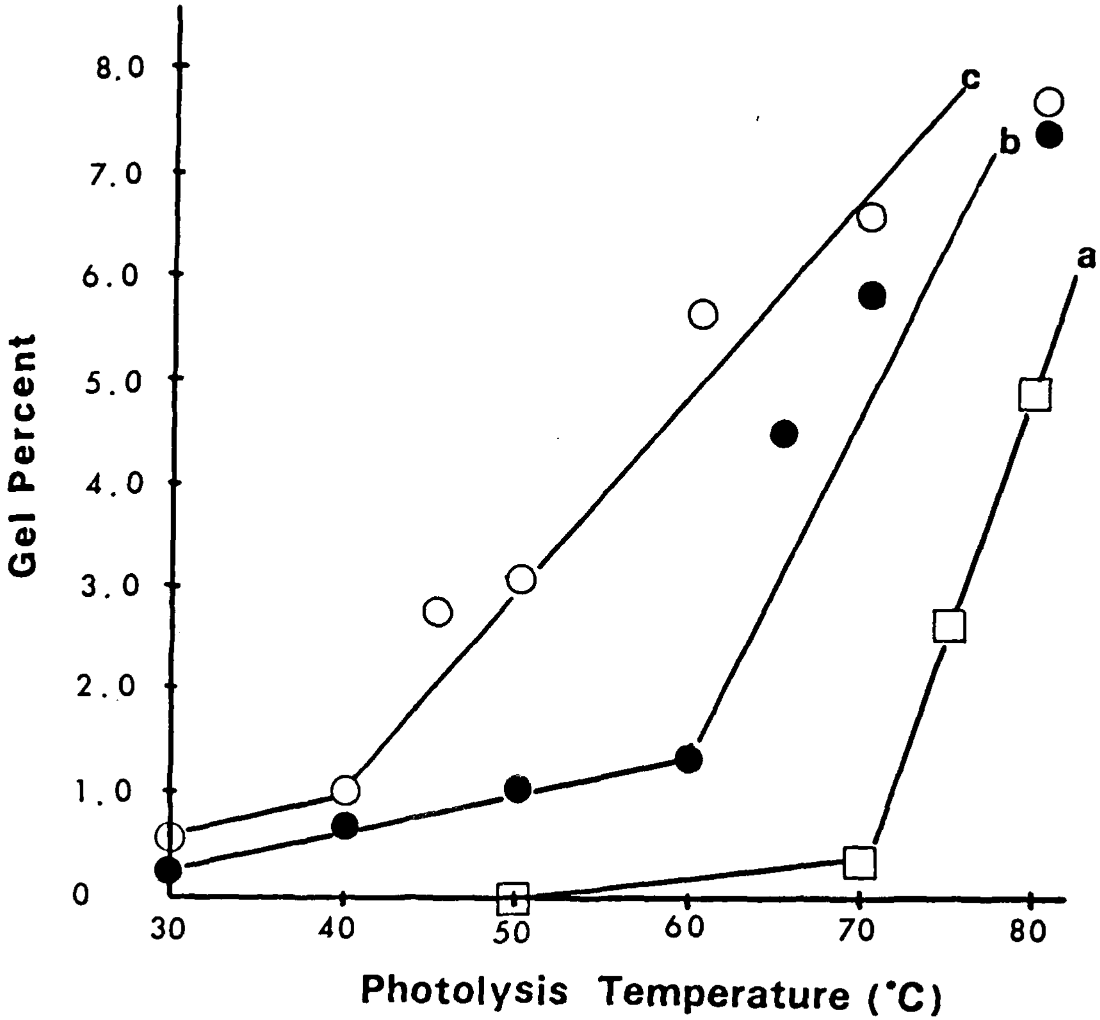

c
b
a
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
Gel Percent
30
40
50
60
70
80
Photolysis Temperature (°C)

Fig. 6

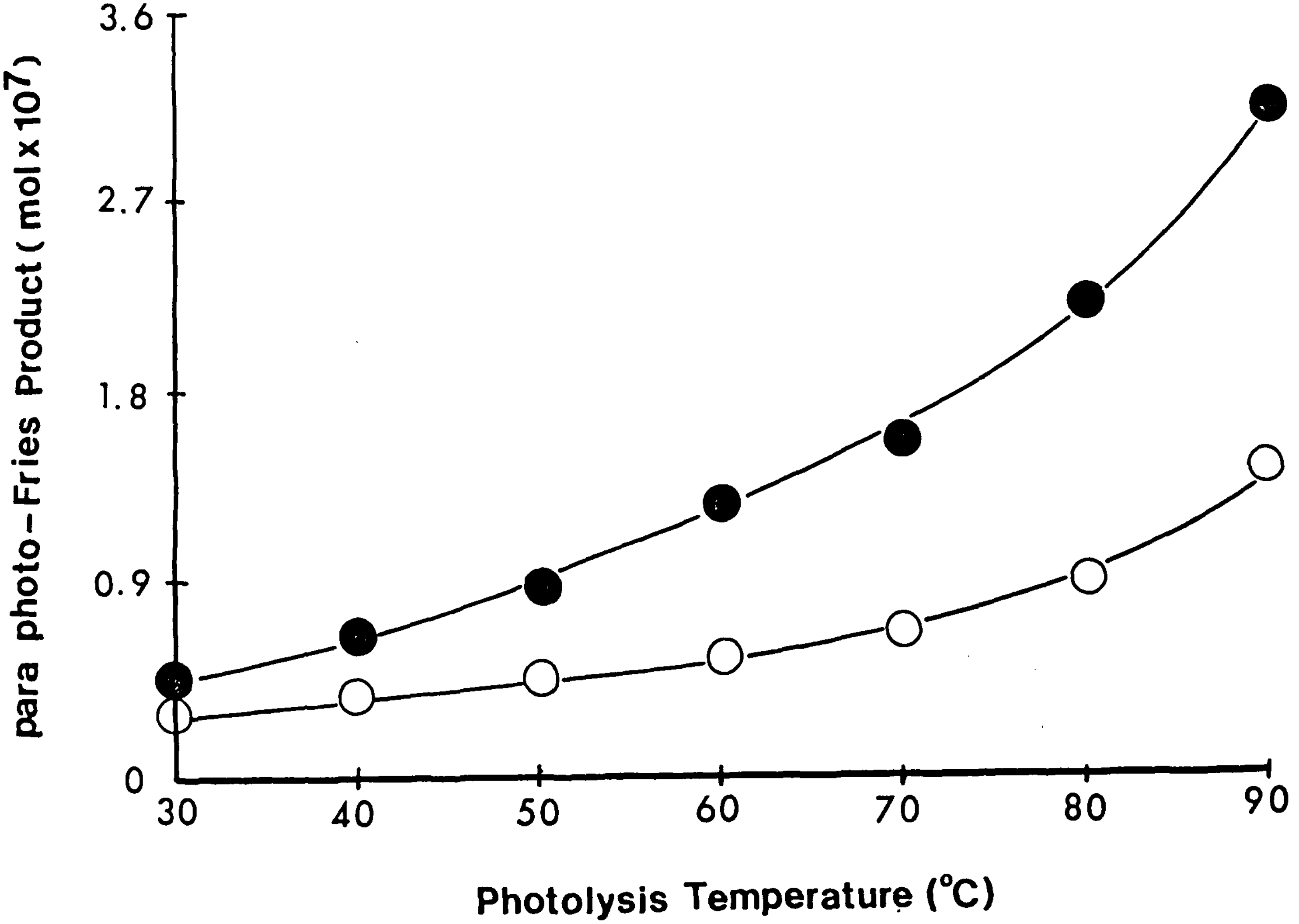

3.6
2.7
1.8
0.9
0
para photo-Fries Product (mol x 10^7)
30
40
50
60
70
80
90
Photolysis Temperature (°C)

Fig. 7

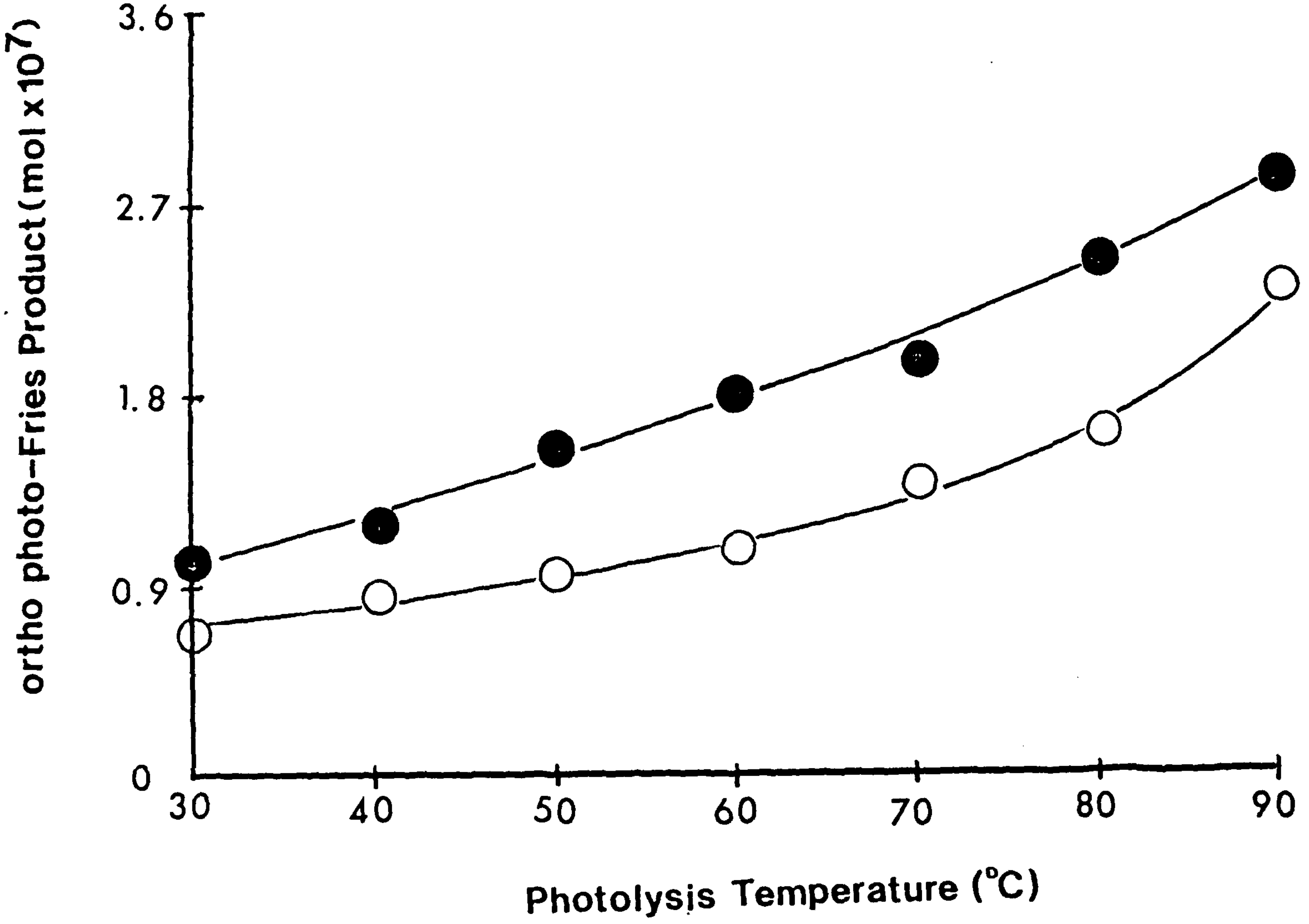

ortho photo–Fries Product (mol x 10^7)
3.6
2.7
1.8
0.9
0
30
40
50
60
70
80
90
Photolysis Temperature (°C)

Fig. 8

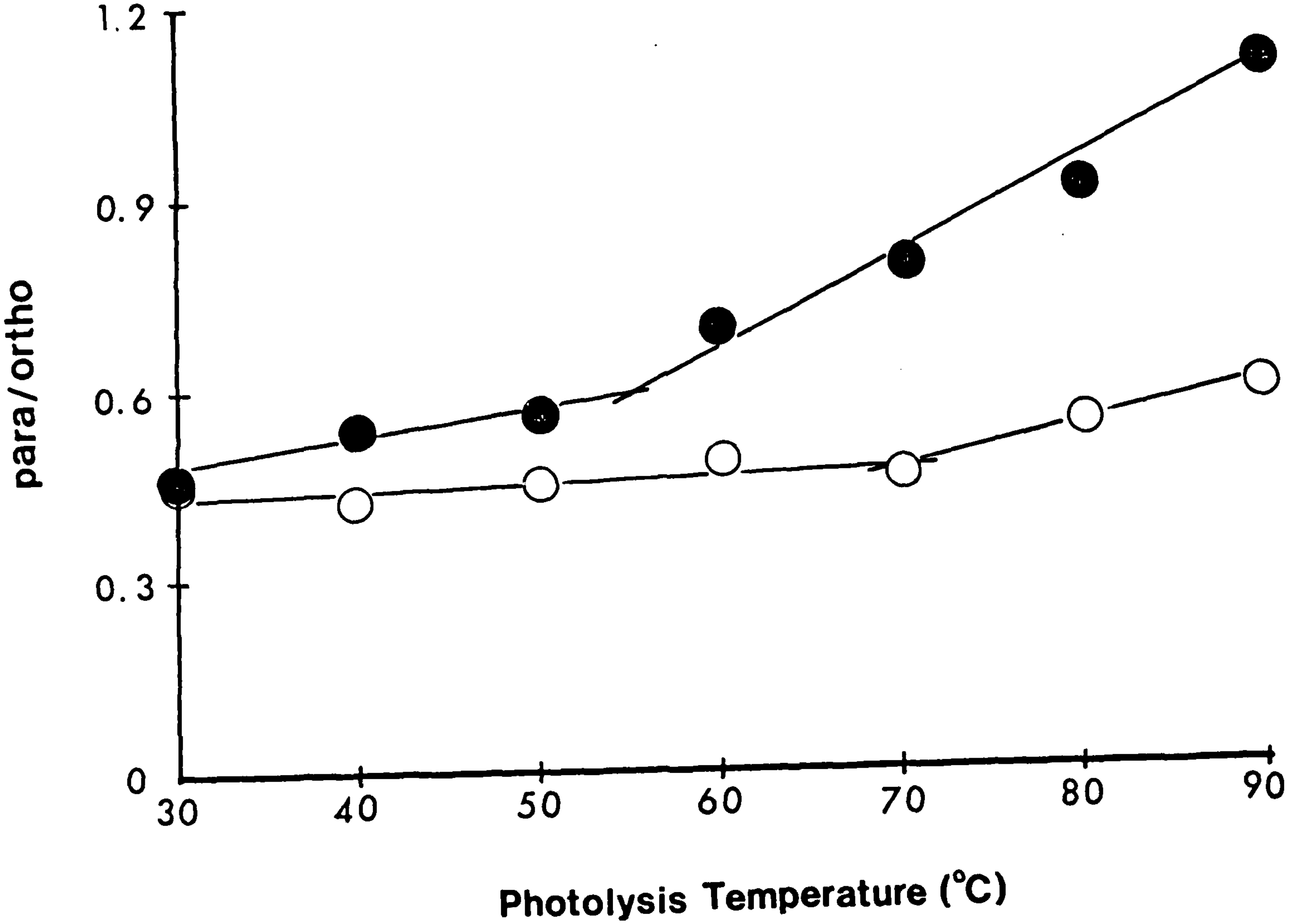
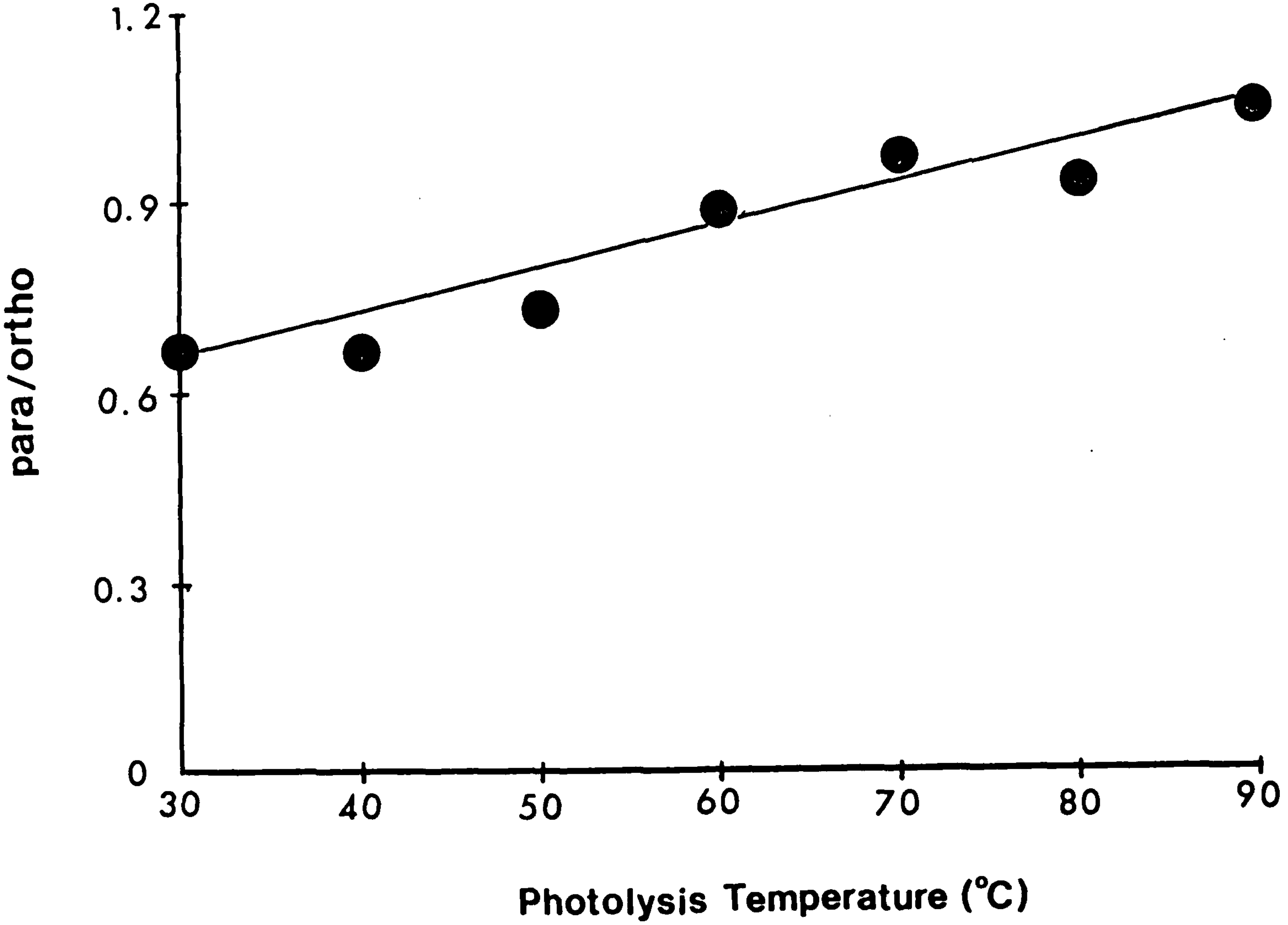

1.2
0.9
0.6
0.3
0
para/ortho
30
40
50
60
70
80
90
Photolysis Temperature (°C)

Fig. 9



1.2
0.9
0.6
0.3
0
para/ortho
30
40
50
60
70
80
90
Photolysis Temperature (°C)

END
9-87
DTIC