



行政院國家科學委員會補助專題研究計畫成果報告

感光型水性 PU 混成樹脂之探討

計畫類別：整合型計畫

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計畫主持人：趙鼎揚 博士

執行單位：中國文化大學應用化學研究所

中華民國：91 年 09 月 30 日

## 一、中文摘要

甲苯二異氰酸鹽 (TDI) 與螢光染料 Fluorescein、聚醚系之多元醇 (PPG2000、PPG700)、二甲醇丙基酸 (DMPA)、Hydroxypropyl acrylate 及其他添加劑反應合成之感光型水性 PU 樹脂之分子結構，已由 FT-IR 光譜證實。

實驗數據顯示感光型水性 PU 樹脂照光成膜之時間，會隨壓克力樹脂 (Hydroxypropyl acrylate) 濃度之增高而縮短，這是因為壓克力樹脂 (Hydroxypropyl acrylate) 濃度之增高會產生較多之自由基因而加速其反應之進行。至於添加光起始劑如 Benzoic 及 Benzophenone 也會使反應加快。感光型水性 PU 樹脂溶液之平均粒徑會隨螢光染料 (Fluorescein) 濃度、壓克力樹脂 (Hydroxypropyl acrylate) 濃度、環氧樹脂濃度和光起始劑濃度之增高而變大，這是因為感光型水性 PU 樹脂分子間之極性基相互作用及 PU 樹脂分子之極性基與水分子彼此之相互作用 (Intermolecular interaction)，而使 PU 樹脂分子之自由體積變大，結果導致感光型水性 PU 樹脂分子之平均粒徑變大。至於此 PU 樹脂薄膜之拉應力會分別隨螢光染料 (Fluorescein) 濃度、壓克力樹脂 (Hydroxypropyl acrylate) 濃度、環氧樹脂濃度和光起始劑濃度之增高而變大，這是因為螢光染料 (Fluorescein)、壓克力樹脂 (Hydroxypropyl acrylate)、環氧樹脂

和光起始劑之官能基會增強 PU 樹脂分子之架橋能力之故。

## 二、英文摘要

Photosensitive-fluorescein polyurethane (PU) ionomer was successfully synthesized at our lab, and the reaction of toluene diisocyanate with polyester, fluorescein, hydroxypropyl acrylate and other major additives to form the structure of this ionomer has been proven by Fourier Transform Infrared Spectra. In aqueous solution, the number average particle size appears to increase respective concentration of epoxy, fluorescein and hydroxypropyl acrylate used to prepare Photosensitive-fluorescein polyurethane ionomer molecules. The reason because the free volume of the photosensitive-fluorescein PU ionomer molecules due to strong intermolecular interaction between hydrophilic groups of these ionomer molecules becomes large. Therefore, the number average particle sizes of these ionomer molecules increase. Furthermore, the addition of benzoin as a photoinitiator to photosensitive-fluorescein polyurethane ionomer molecule

results in increasing the average particle size of this ionomer molecule. This is due to increased free volume resulting from strong intermolecular interaction between hydrophilic groups of ionomer molecules. For self-cured films made by photosensitive-fluorescein polyurethane ionomer, the tensile strength is seen to increase with increasing concentration of epoxy, fluorescein and hydroxypropyl acrylate, respectively. This may be attributed to increased crosslinking due to strong intermolecular interaction between photosensitive-fluorescein polyurethane ionomer molecules themselves. However, the addition of benzoin as a photoinitiator to photosensitive-fluorescein polyurethane ionomers results in increasing the tensile strength of these ionomers as well.

### 三、計畫緣由與目的

特用化學品乃是一群具有特殊機能，多品種，少量生產技術密集及高附加價值之化學品，其使用範圍相當廣泛，發展潛力也相當雄厚，因此奉行行政院經濟建設委員會列為公元 2000 年之十大新興工業。我國合成樹脂接著劑工業和染料工業經過多年努力，不僅產品方面力求

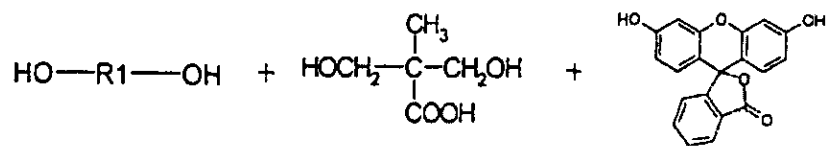
生產成本合理化、多元化之外，在市場方面也積極開拓國際市場，藉以降低國內市場競爭壓力，顯然合成樹脂接著劑工業與染顏料工業已經朝向技術密集方向邁進，也成為特用化學品主要的一環。不過近年來由於環保意識高漲，為了減少對環境造成公害，合成樹脂接著劑與染顏料工業正逐步由溶劑型轉變為水溶劑型，如此不但可以減少對環境造成污染，並可以增強在國際市場的競爭力。

一般傳統溶劑型 PU 樹脂之應用雖然已趨於相當成熟，但近年來政府環保法規及安全條件的要求日漸嚴格，加上溶劑價格的起伏會直接影響樹脂的生產成本。為使我國染顏料工業能開拓國際市場，以降低國內市場競爭壓力，在染顏料工業已邁向技術密集方向的同時，藉由水性 PU 樹脂易於染色的特性，將染料引入 PU 樹脂中，不但可以增強在國際市場的競爭力，還可以合乎工業減廢的要求，亦可藉著樹脂之接著力增強染料的能力，有助於染料工業的技術升級。

一般而言水性 PU 樹脂成膜時必須利用烘箱加熱成膜或長時間乾燥成膜，由於成膜時間不夠快速，而且會受到環境種種條件之限制，因此將感光材料加入水性 PU 樹脂，在紫外線照射下可縮短水性 PU 樹脂成膜的時間，減少水性 PU 樹脂成膜應用時受到氣候及環境的影響，有利於水性 PU 樹脂的應用性。

為進一步提昇我國特用化學品工業之技術，及配合國際發展低污

染性水性 PU 混成樹脂之趨勢，此時更應進行感光行水性 PU 混成樹脂之研究與開發。本論文主要是合成感光型水性 PU 混成樹脂，並對其物性做較深入之探討。甲苯二異氰酸鹽與螢光染料及其他添加劑反應成感光型水性 PU 混成樹脂之分子結構如下：

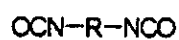


Polypropylene Glycol Dimethylol Propionic Acid Fluorescein

(PPG)

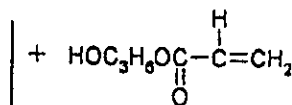
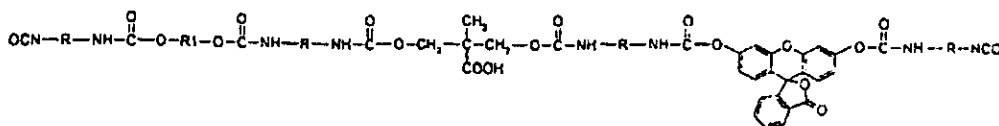
(DMPA)

+

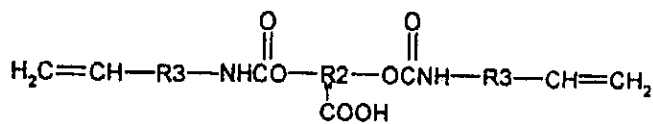


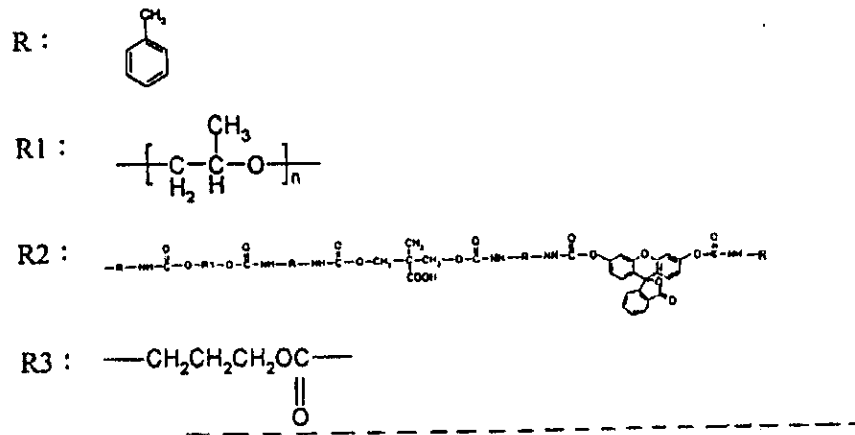
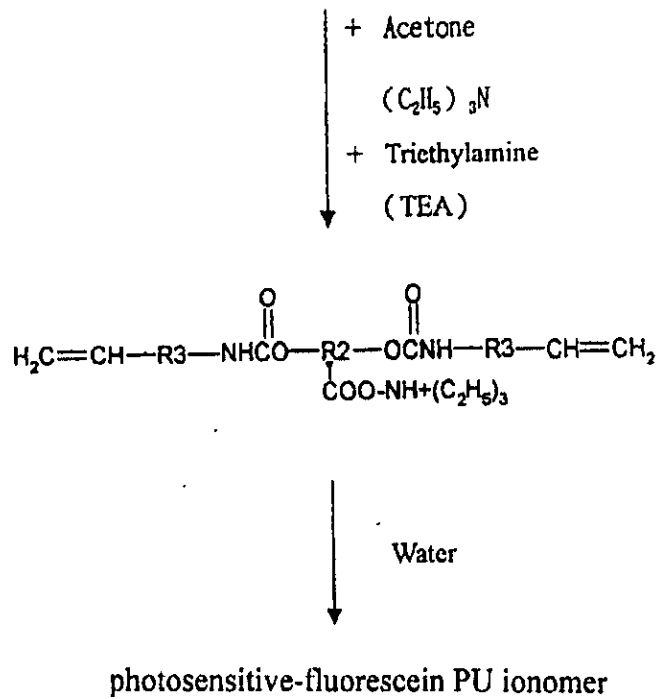
Toluene Diisocyanate

(TDI)



Hydroxypropyl Acrylate





#### 四、研究方向及成果

##### 研究方法

##### 4.1 實驗分析儀器

##### (1) 紅外線光譜儀

FTIR, Model 1605, Prekin Elmer, USA

##### (2) 粒徑測定儀

電器泳動光散亂光度記, ELS-800, 大塚電子, 日本



### (3)機械強度測定儀

GT-7010-A2，微電腦拉力試驗，高鐵科技股份有限公司(Gotech Testing Machines Inc)

### (4)輸送帶紫外線照射烘乾機

## 4.2 實驗藥品

### (1)聚醚(Polyether Glycol)

PTMEG (Polytetramethylene Glycol)，Mw=2000

PPG 700 (Polypropylene Glycol)，Mw=700

NPG (Polypropylene Glycol)，Mw=104

台精化工公司

### (2)1，4-丁二醇(1，4-Butane Diol )

$(\text{CH}_2)_4(\text{OH})_2$ ，Mw= 90

台精化工公司

### (3)二甲醇基丙酸(Dimethylol Propionic Acid，DMPA)

$\text{CH}_3\text{C}(\text{CH}_2\text{OH})_2\text{COOH}$ ，Mw=134.13

Alcolac Industrial Chemical，USA

### (4)二甲基乙醯胺(N，N-Dimethyl Acetamide，DMAC)

$\text{C}_4\text{H}_9\text{NO}$ ，Mw=87.12

Riedel-de Hean，Germany

(5) 螢光染料 Fluorescein

$C_{20}H_{12}O_5$  , Mw=236.22

Lancaster , England

(6) 環氧樹脂(Epory Resin)

BE-501 E. W. =1000

長春公司

(7) 甲苯二異氰酸酯(Toluene Diisocyanate , TDI)

$C_9H_6O_2N_2$  , Mw=174.16

台精化工公司

(8) 丙酮(Acetone)

$H_3COCH_3$  , Mw=58.08

和光純藥工業株式會社

(9) Hydroxypropyl Acrylate

$C_6H_{10}O_3$  , Mw=130.14

Aldrich chemical company , USA

(10) 三乙基胺(Triethylamine , TEA)

$(C_2H_5)_3N$  , Mw=101.19

Riedel-de Hean , Germany

(11) 二苯甲酮(Benzophenone)

$C_6H_5COC_6H_5$  , Mw=182.21

New jersey , USA

中國文化大學提供

#### 4. 3 感光型水性 PU 混成樹脂之製備

##### 4. 3. 1 實驗步驟：

(1)將 0.007 當量的 Polytrimethylene glycol (PTMEG)、0.004 當量的聚丙二醇 700(PPG 700)、0.0001 當量的新戊醇(NPG) 、0.003 當量的 1,4-丁二醇(1,4-B.G. ) 、0.001 當量的 Fluorescein 0.001 當量的環氧樹脂(epoxy resin)及 0.002 當量的二甲醇基丙酸(DMPA) , 混合置入 1000 毫升的四頸瓶中 , 再加入 20 克的二甲基乙醯胺(DMAc) , 然後加熱攪拌。

(2)溫度升至 70~75°C 時 , 分批加入適量的甲苯二異氰酸(TDI)後 , 在溫度 75~80°C 及轉速 500rpm 的攪拌速度下進行溶液聚合反應 , 直到 IR 光譜顯示異氰酸基(-NCO-)含量消失或不在減少為止。

(3)將 65 克的丙酮(Acetone)加入上述溶液中並控制溶液的黏度 , 進行反應 10 分鐘後 , 分別將 0.001 當量的壓克力(Hydroxypropyl acrylate)和 0.03 當量的三乙基胺(Triethyl amine)加入溶液中反應。

(4)將 0.6% 光起始劑(Benzophenone)加入上述溶液中 , 攪拌 10 分鐘後 , 在加入 170 克的去離子水 , 則可獲得感光型水性 PU 混成樹脂。

(5)利用減壓蒸餾去除溶液中的丙酮。改變螢光染(Fluorescein)、壓克力樹脂(Hydroxypropyl acrylate)、環氧樹脂(Epoxy resin)的濃度(0.001~0.003 當量)及光起始劑(Benzophenone)的濃度(1%~5%)而固定其他組成成份，可調配成一系列不同種類與濃度之感光型樹脂溶液。

## 五、結果與討論

### 5.1 IR 光譜圖之探討

甲苯二異氰酸酯 (Toluene diisocyanate)，壓克力樹脂 (Hydroxypropyl acrylate) 和螢光染料 (Fluorescein) 之 IR 光譜圖分別說明在圖 1 至圖 3。甲苯二異氰酸酯與聚醚 (Polypropylene glycol)，螢光染料 (Fluorescein)，壓克力樹脂 (Hydroxypropyl acrylate) 和其他添加劑反應形成末端為 NCO 之感光型 PU 預聚合物之光譜圖說明在圖 4。比較圖 4 與圖 1-3 IR 光譜顯示 NHCO 基的吸收峰 ( $1537\text{ cm}^{-1}$ )，NH 基的吸收峰 ( $3340\text{ cm}^{-1}$ )，C=O 基的吸收峰 ( $1720\text{ cm}^{-1}$ )，RCH=CH<sub>2</sub> 基的吸收峰 ( $1633\text{ cm}^{-1}$ )，CH<sub>2</sub>-O-CO- 基的吸收峰 ( $1451\text{ cm}^{-1}$ ) 和 C-O 基的吸收峰 ( $1016\text{ cm}^{-1}$ ) 的出現及 NCO 基的吸收峰 ( $2275\text{--}2375\text{ cm}^{-1}$ ) 的減弱與消失，可以證明感光型 PU 預聚合物含有聚醚、壓克力樹脂、螢光染料及甲苯二異氰酸酯等成份。就 IR 光譜之數據分析而言，甲苯二異氰酸酯與壓克力樹脂、螢光染料、

環氧樹脂及其他添加劑之反應是可能形成感光型水性 PU 混成樹脂。

5.2 分別改變壓克力樹脂 (Hydroxypropyl acrylate)，螢光染料 (Fluorescein) 和環氧樹脂 (Epoxy resin; BE-501, E. W=1000) 之濃度對感光型水性 PU 混成樹脂溶液之平均粒徑影響之情形：

分別改變壓克力樹脂，螢光染料和環氧樹脂之濃度而固定其他組成成分，結果發現感光型水性 PU 混成樹脂溶液之平均粒徑，會隨壓克力樹脂或是螢光染料或是環氧樹脂濃度之增高而變大，如圖 5 所示，這是因為水性 PU 分子間 (intermolecular) 的作用 (interaction) 增強，使得水性 PU 分子的自由體積變大，而導致水性 PU 分子的平均粒徑增大。在相同的實驗條件下，增高光起始劑 (Benzion) 的濃度，也會導致感光型水性 PU 分子的平均粒徑變大，如圖 6 所示，原因與圖 5 的說明相同。

5.3 分別改變光起始劑 (benzophenone, benzoin) 之濃度而固定壓克力樹脂之濃度對感光型水性 PU 混成樹脂 UV 照射時間影響之情形：

分別改變光起始劑 benzophenone 和 benzoin 而固定其他組成成分，結果發現感光型水性 PU 混成樹脂 UV 照射時間會隨光起始劑濃度之增高而變小，如圖 7 所示，這是因為光起始劑的濃度增高會使壓克力樹脂 C=C 雙鍵斷裂形成自由基，這些自由基會加速水性 PU 分子的架橋 (crosslinking) 或是硬化 (cured)。

5.4 改變壓克力樹脂之濃度而固定其他組成成份對感光型水性 PU 混成樹脂 UV 照射時間之影響：

改變壓克力樹脂 (Hydroxypropyl acrylate) 之濃度，而固定其他組成成份，結果發現感光型水性 PU 混成樹脂 UV 照射時間會隨壓克力樹脂濃度之增高而變小，如圖 8 所示，這是因為增高壓克力樹脂之濃度會形成較多自由基，這些自由基會加速水性 PU 分子之架橋或是硬化。

5.5 分別改變環氧樹脂，螢光染料，壓克力樹脂和光起始劑濃度對感光型水性 PU 混成樹脂薄膜拉應力(tensile strength)影響之情形：

分別改變環氧樹脂，螢光染料，壓克力樹脂和光起始劑濃度而固定其他組成成分，結果發現感光型水性 PU 混成樹脂薄膜的拉應力會隨著環氧樹脂的濃度或是螢光染料的濃度或是壓克力樹脂的濃度或是光起始劑濃度之增高而變大，如圖 9 和圖 10 所示，原因是因為感光型水性 PU 混成樹脂分子的極性基增多，這些極性基會使水性 PU 分子間 (intermolecular) 的作用力增強，結果導致感光型水性 PU 混成樹脂薄膜的拉應力增強。至於感光型水性 PU 樹脂含環氧樹脂薄膜的拉應力會比水性 PU 樹脂含壓克力樹脂或是螢光染料的拉應力強。這是因為含環氧樹脂的水性 PU 樹脂分子間的作用力較強之故(含有較多的極性基)。值得注意的是：增高光起劑的濃度也會增強感光型水性 PU 分子

薄膜的拉應力，原因是因為光起始劑會使壓克力 C=C 雙鍵斷裂形成較多的自由基，這些自由基會加速水性 PU 分子的架橋或是硬化，結果導致水性 PU 樹脂薄膜的拉應力增強。

## 六、設備

1. 甲苯二異氰酸酯與聚醚，壓克力樹脂，螢光染料，環氧樹脂和其他添加劑反應成感光型水性 PU 混成樹脂分子的結構已經 IR 光譜證實。
2. 感光型水性 PU 混成樹脂分子溶液的平均粒徑會分別隨環氧樹脂濃度或是壓克力樹脂濃度或是螢光染料濃度之增高而變大，這是因為水性 PU 分子的自由體積受水性 PU 分子間的作用力增強而變大之故。
3. 感光型水性 PU 混成樹脂 UV 照射時間會分別隨光起始劑和壓克力樹脂濃度之增高而變小，原因是因為壓克力 C=C 雙鍵斷裂形成較多的自由基，會加速溶液中感光型水性 PU 混成樹脂乾躁成膜。
4. 感光型水性 PU 混成樹脂薄膜的拉應力會分別隨環氧樹脂，螢光染料和光起始劑濃度之增高而增強，原因是因為水性 PU 分子間的作用力增強之故。

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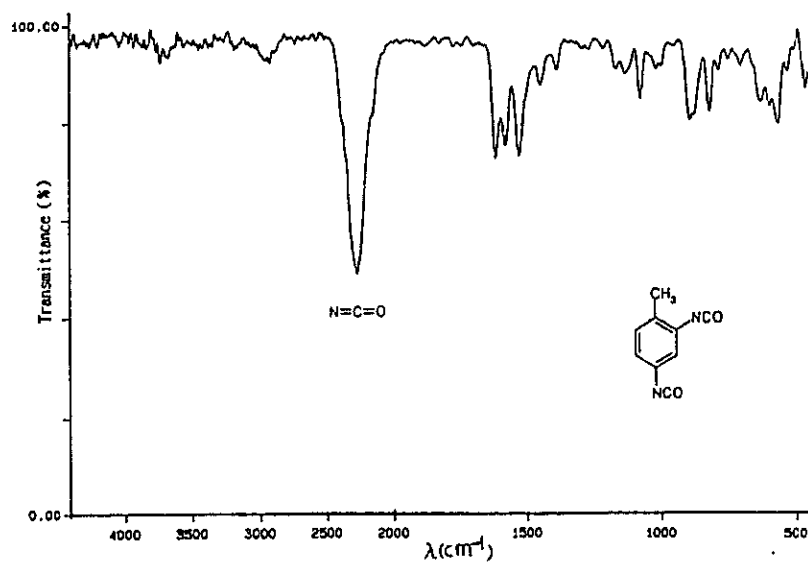


Figure 1 Spectra of toluene diisocyanate at  $25 \pm 0.05^\circ\text{C}$ .



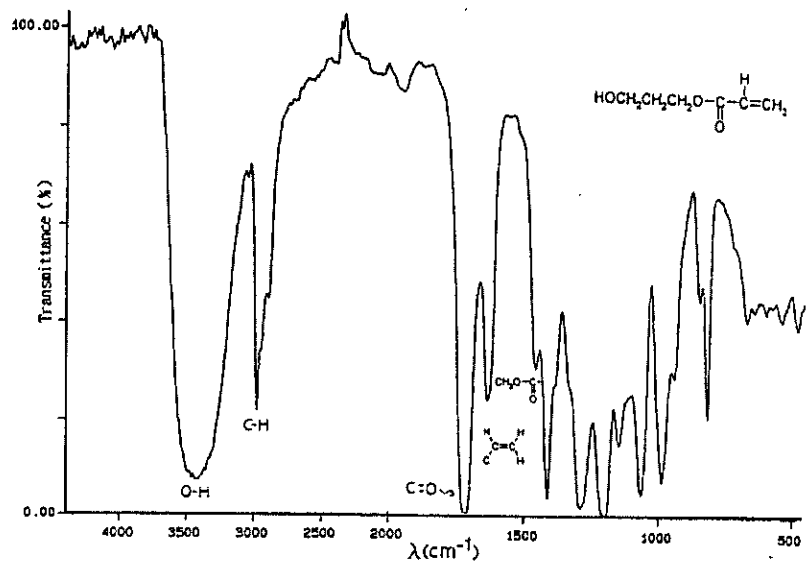


Figure 2 Spectra of hydroxypropyl acrylate at  $25 \pm 0.05^\circ\text{C}$ .

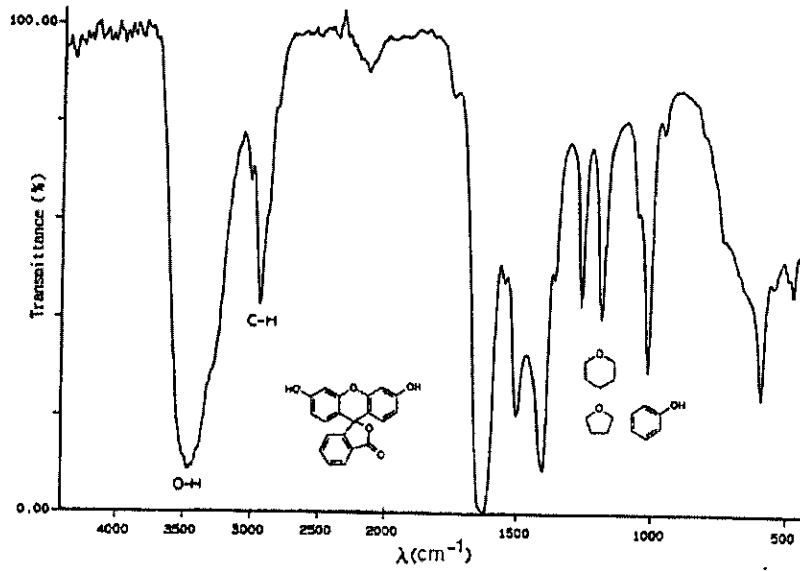


Figure 3 Spectra of fluorescein at  $25 \pm 0.05^\circ\text{C}$ .

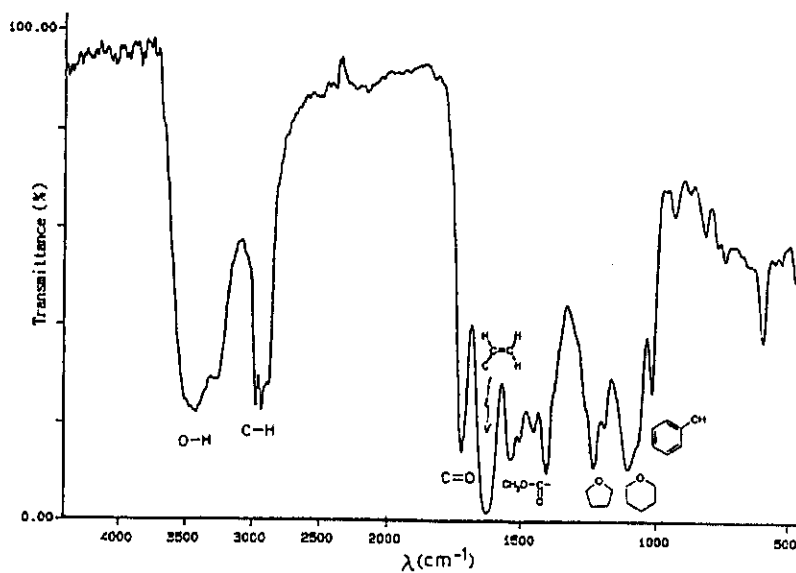


Figure 4 Spectra of photosensitive-fluorescein PU prepolymer formed after 2h reaction , at 25±0.05°C.

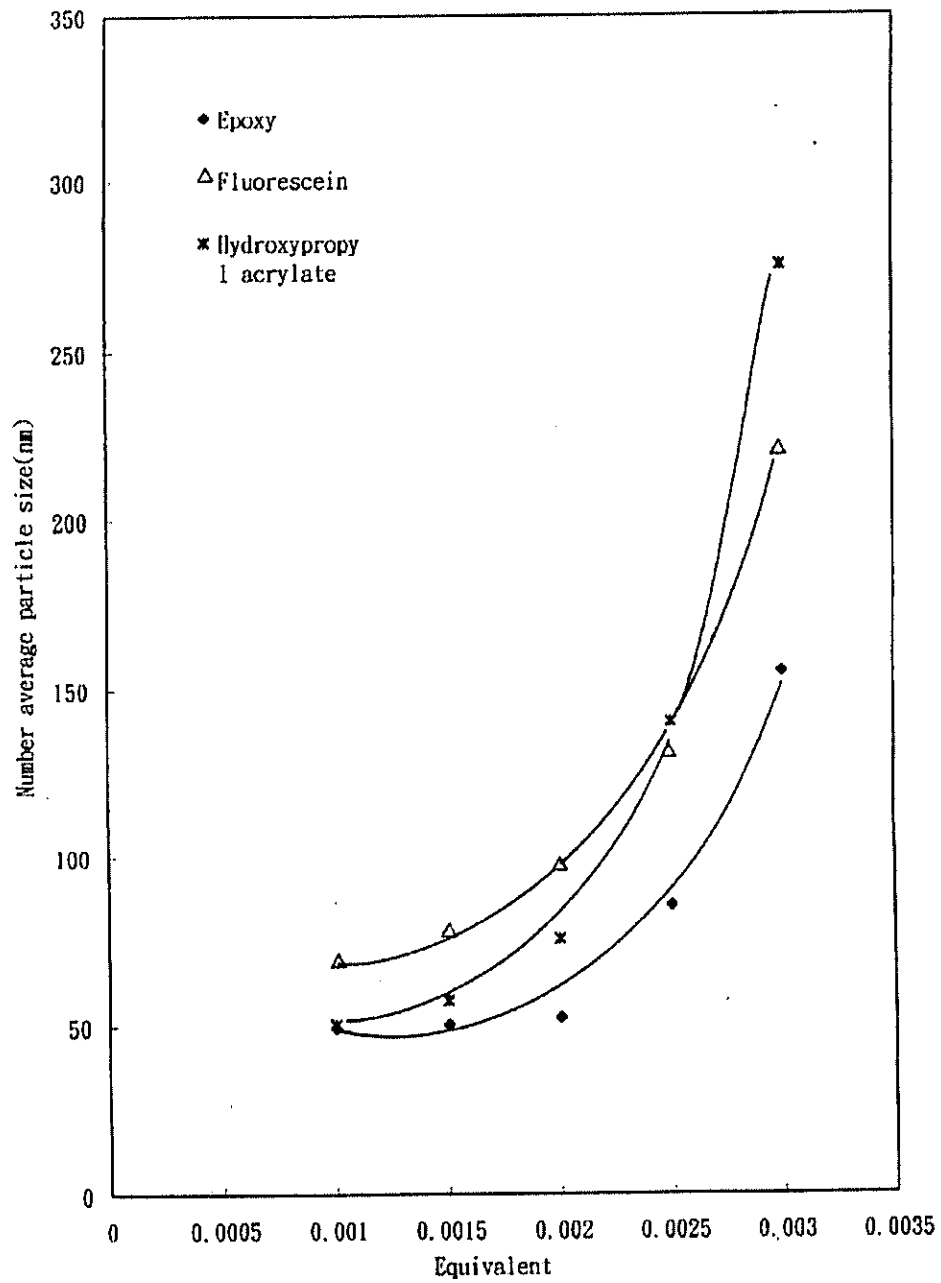


Fig5 Number average particle size versus the respective concentration of epoxy, fluorescein and hydroxypropyl acrylate used to prepare photosensitive-fluorescein polyurethane ionomer, at  $25 \pm 0.05^\circ\text{C}$ .

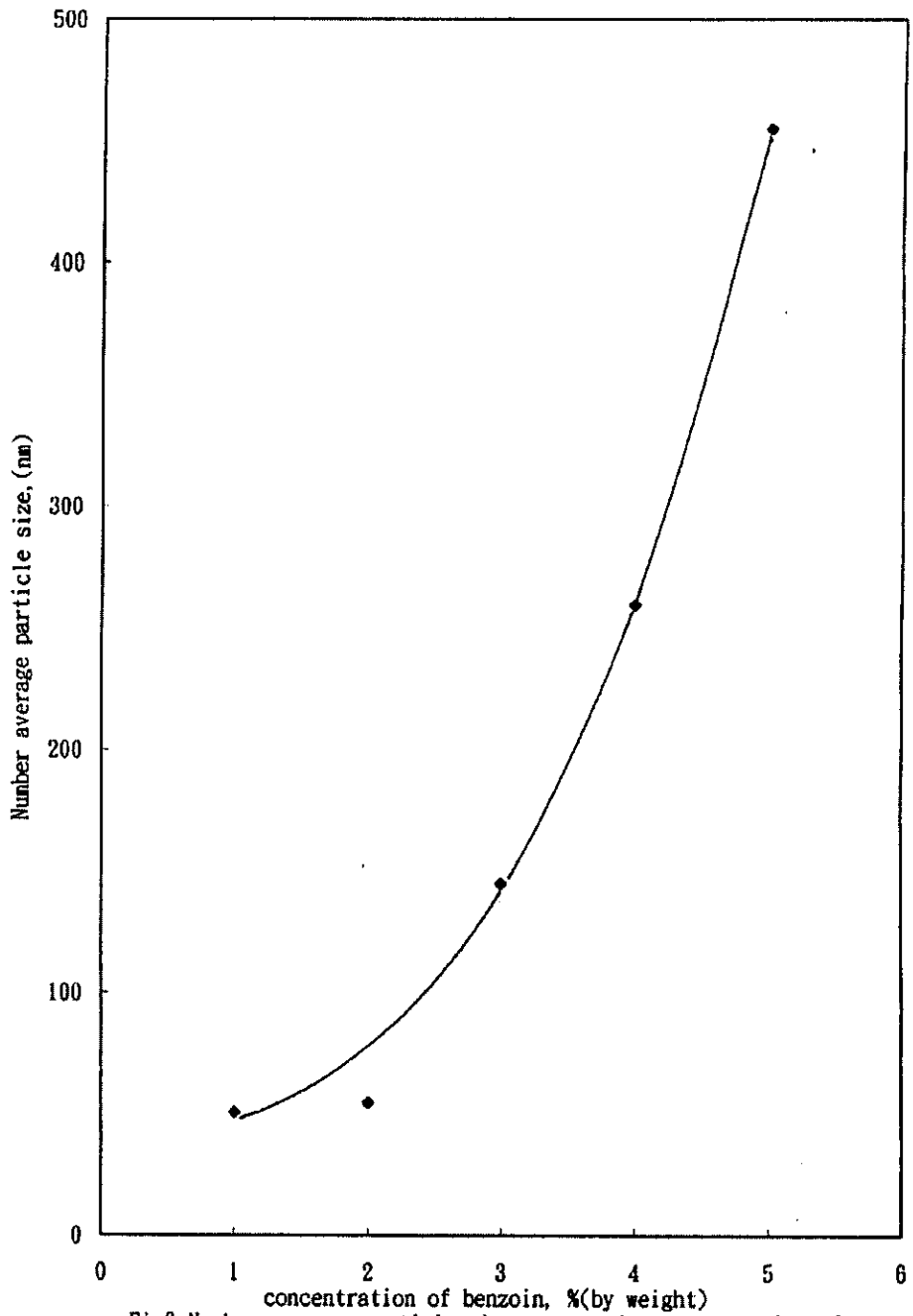
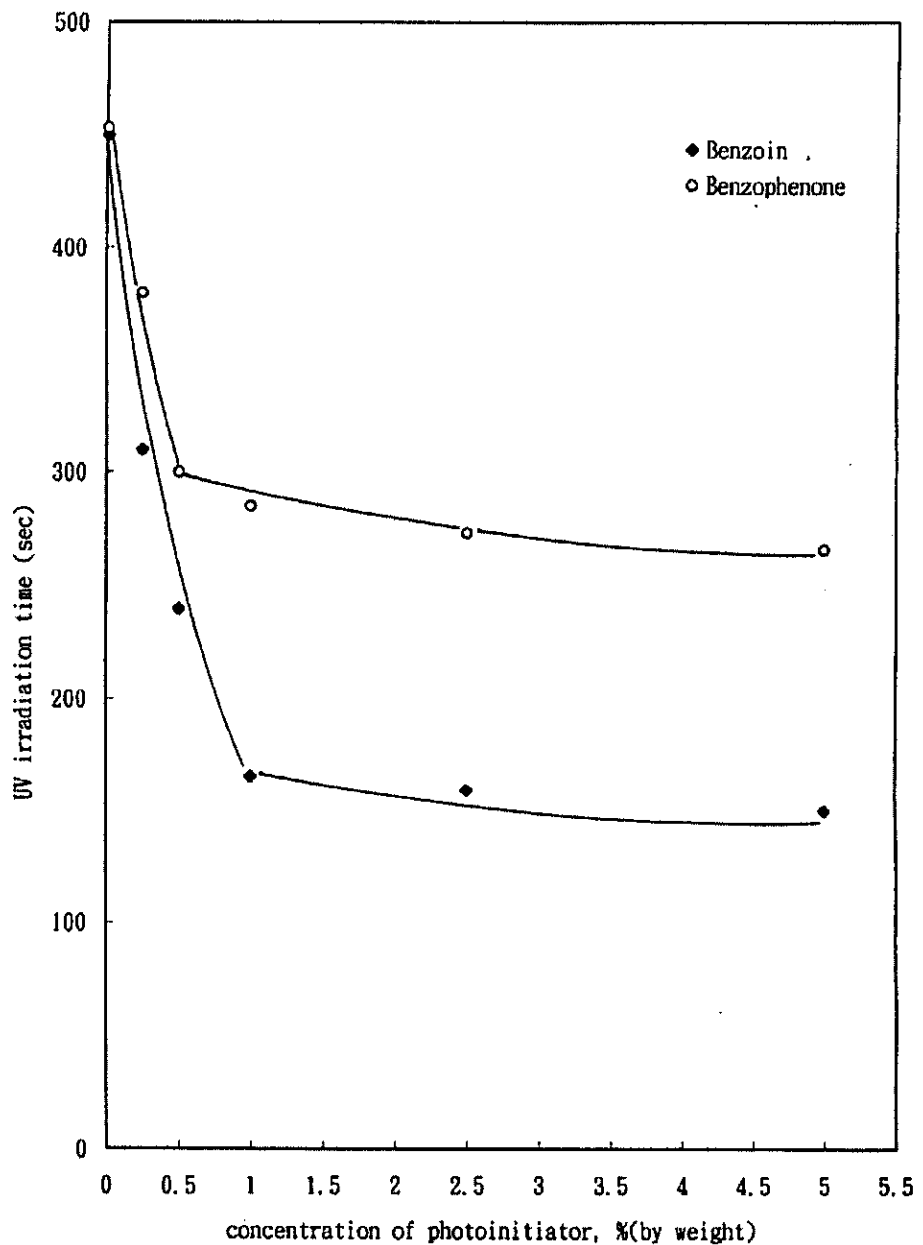
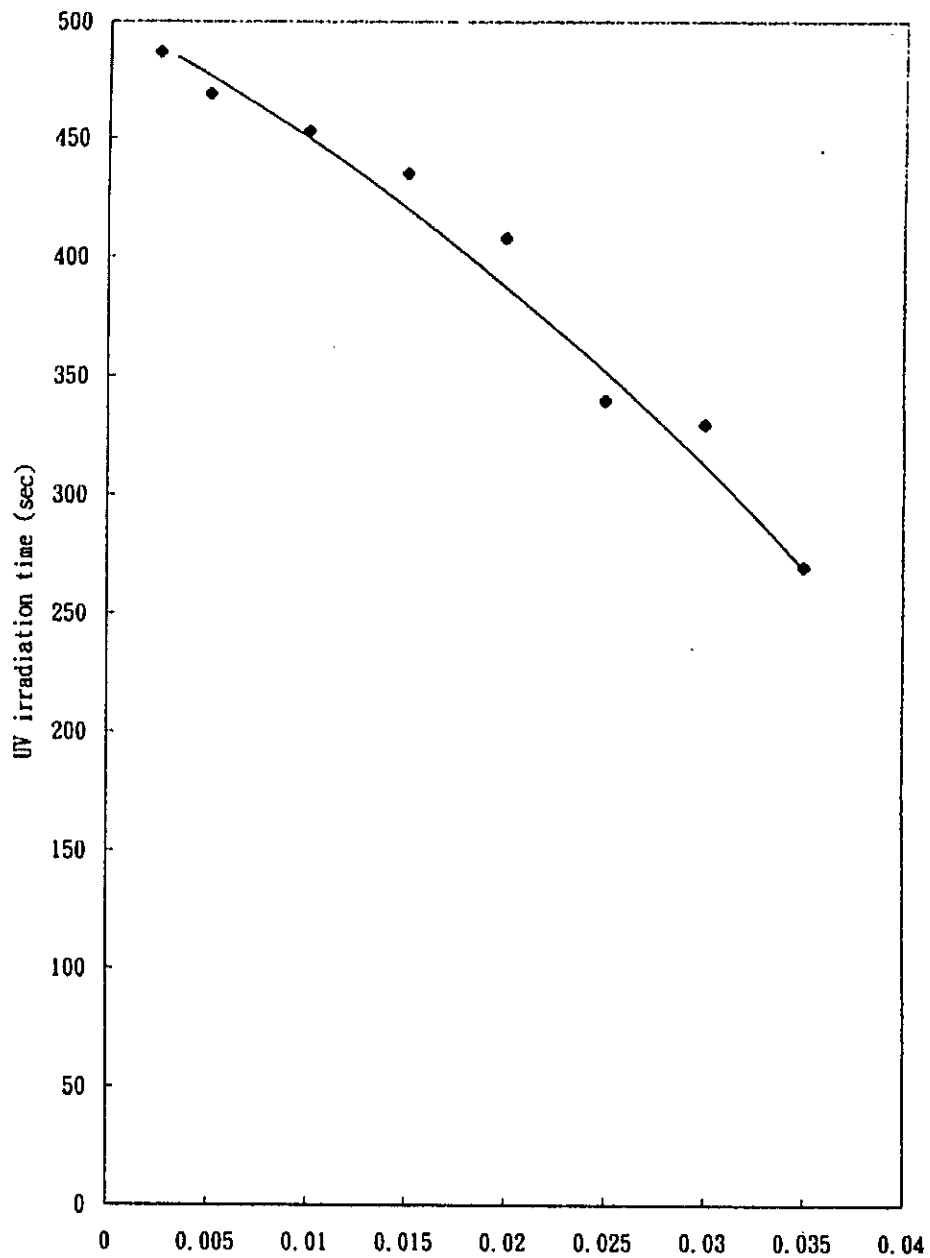


Fig6 Number average particle size versus the concentration of benzoin used to prepare photosensitive-fluorescein polyurethane ionomer, at  $25 \pm 0.05^\circ\text{C}$ .



concentration of photoinitiator, %(by weight)  
 Fig7 UV irradiation time versus the respective concentration of benzoin and benzophenone in the presence of a fixed concentration of 0.01 equivalent of hydroxypropyl acrylate used to prepare photosensitive-fluorescein polyurethane ionomer.



Equivalent of hydroxypropyl acrylate  
Fig8 UV irradiation time versus the concentration of  
hydroxypropyl acrylate used to prepare photosensitive-  
fluorescein polyurethane ionomer

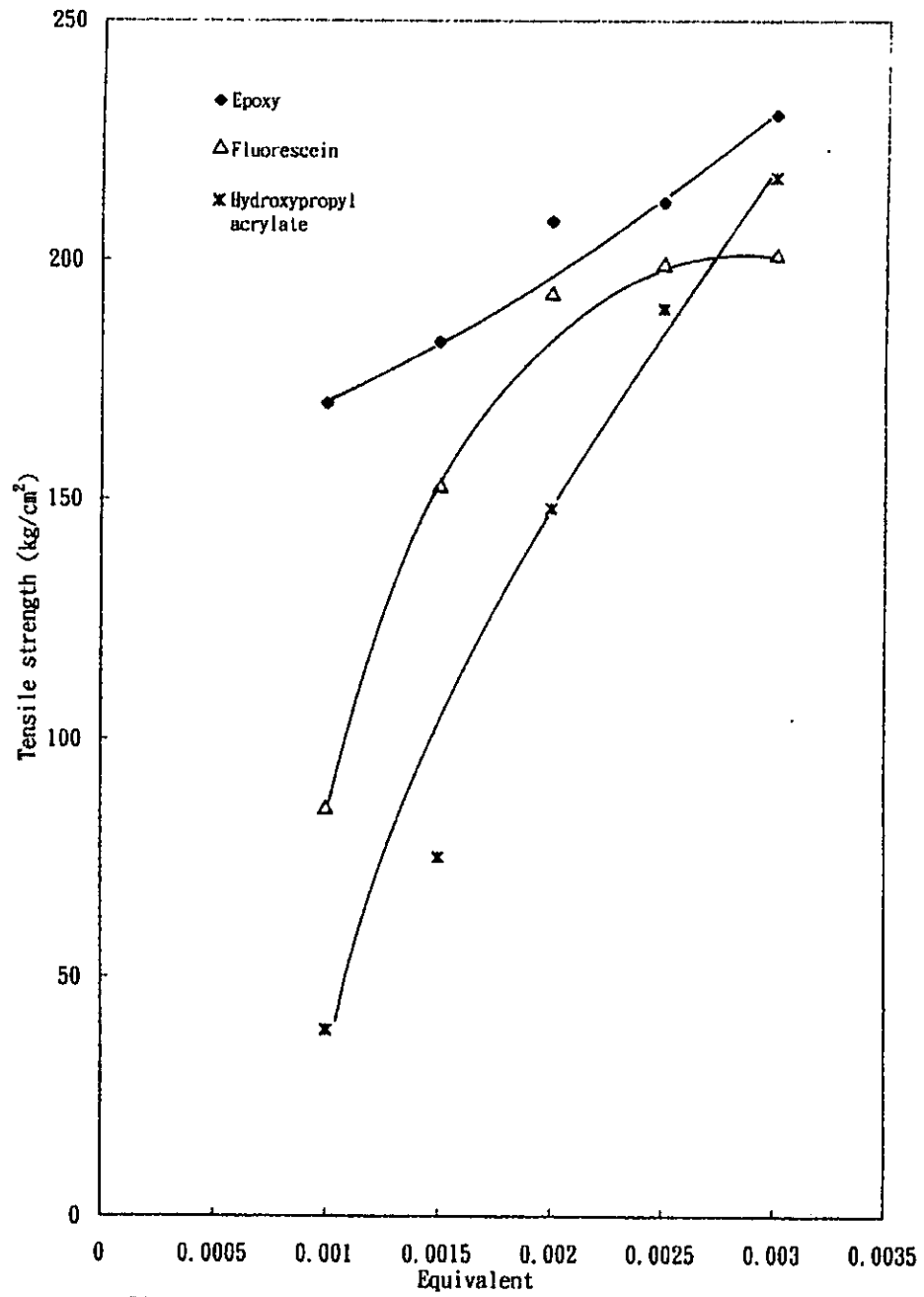


Fig9 Tensile strength versus the respective concentration of epoxy, fluorescein and hydroxypropyl acrylate used to prepare photosensitive-fluorescein polyurethane ionomer, 25± 0.05°C.

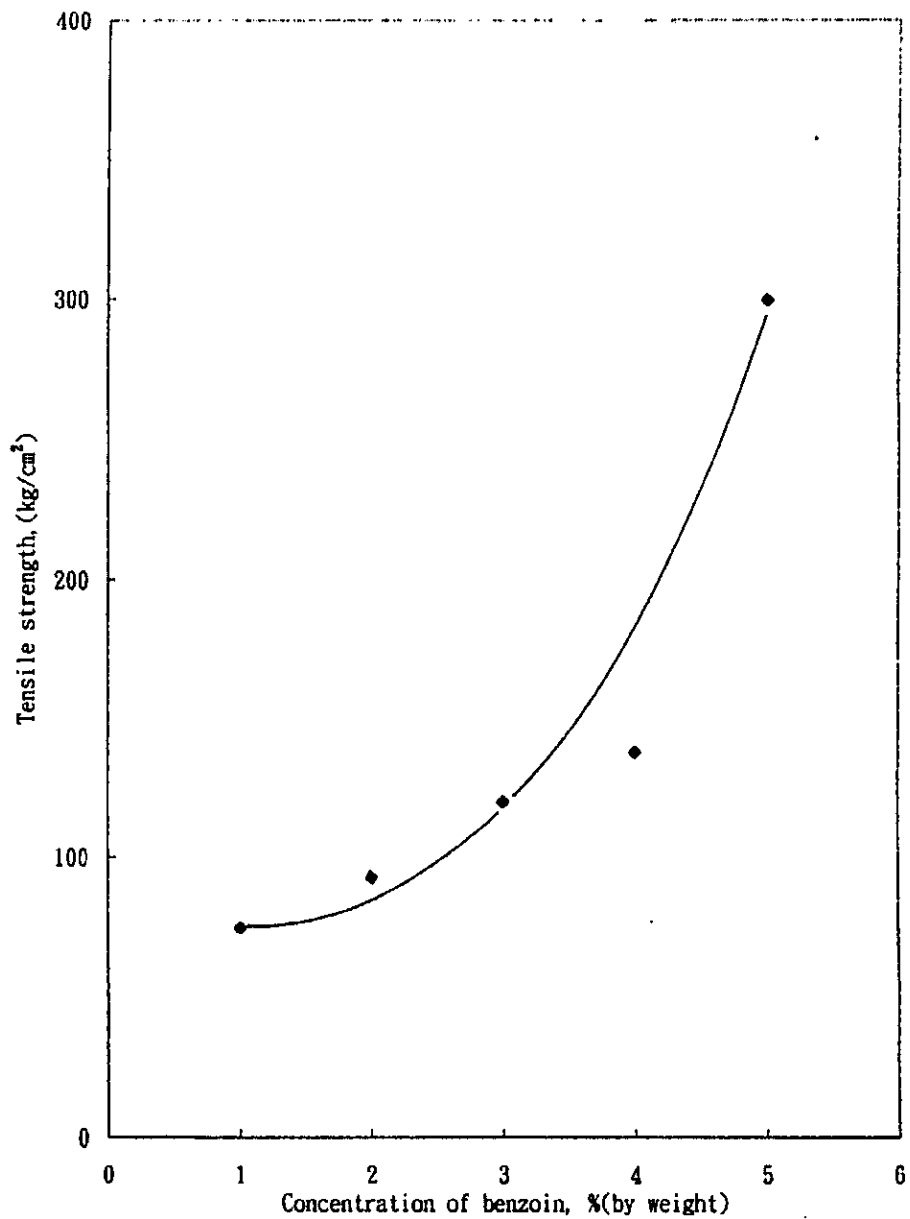


Fig10 Tensile strength versus the concentration of benzoin used to prepare photosensitive-fluoresin polyurethane ionomer, 25± 0.05°C.



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## EDITOR:

Eric Baer  
Dept. of Macromolecular Science  
Case Western Reserve University  
Cleveland, OH 44106  
Tel. 216-368-4203  
Fax: 216-368-6329

## CO-EDITOR:

Anne Hiltner  
Dept. of Macromolecular Science  
Case Western Reserve University  
Cleveland, OH 44106  
Tel. 216-368-4186  
Fax: 216-368-6329

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## ASSOCIATE EDITORS:

Rabeh H. Elleithy  
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PolyOne Corporation  
33587 Walker Road  
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Fax: (440) 930-1644

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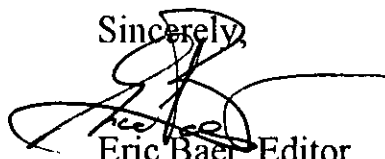
Dear Prof. Chao:

Your manuscript on "A STUDY OF PHOTSENSITIVE FLUORESCIN POLYURETHANE IONOMER" (I.D. No. 11,297) has been carefully reviewed and I am delighted to inform you that it will be published in a future edition of the Journal of Applied Polymer Science.

Enclosed please find a publication agreement to sign and return to me at your earliest convenience. If it is possible, I would like to ask you for a diskette of the final manuscript. May I take this opportunity to thank you for contributing your work to our journal.

With best regards, I am

Sincerely,



Eric Baer, Editor  
Journal of Applied Polymer Science

EB:pas

## Abstract

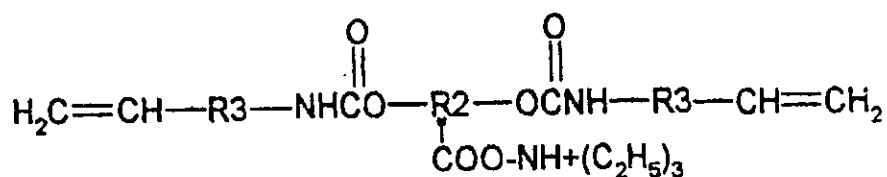
Photosensitive-fluorescein polyurethane (PU) ionomer was successfully synthesized at our lab, and the reaction of toluene diisocyanate with polyester, fluorescein, hydroxypropyl acrylate and other major additives to form the structures of these ionomer has been proven by Fourier Transform Infrared Spectra. For a dilute concentration of photosensitive-fluorescein polyurethane ionomer molecule in aqueous solution, the fluorescence study exhibits fluorescence at around 508nm. In aqueous solution, the number average particle size appears to increase with increasing respective concentration of epoxy, fluorescein and hydroxypropyl acrylate used to prepare Photosensitive-fluorescein polyurethane ionomer molecules. The reason because the free volume of photosensitive-fluorescein PU ionomer molecules due to strong intermolecular interaction between hydrophilic groups of these ionomer molecules becomes large. Therefore, the number average particle sizes of these ionomer molecules increase. Furthermore, the addition of benzoin as a photoinitiator to photosensitive-fluorescein polyurethane ionomer molecule results in increasing the average particle size of this ionomer molecule. This is due to increased free volume resulting from strong intermolecular interaction between hydrophilic groups

of ionomer molecules. For self-cured films made by photosensitive-fluorescein polyurethane ionomer, the tensile strength is seen to increase with increasing concentration of epoxy, fluorescein and hydroxypropyl acrylate, respectively. This may be attributed to increased crosslinking due to strong intermolecular interaction between photosensitive- fluorescein polyurethane ionomer molecules themselves. However, the addition of benzoin as a photoinitiator to photosensitive-fluorescein polyurethane ionomers results in increasing the tensile strength of these ionomers as well.

## **Introduction**

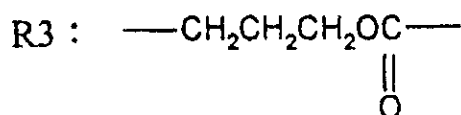
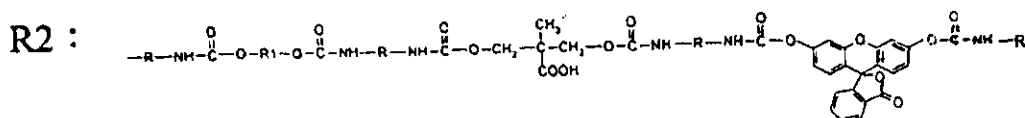
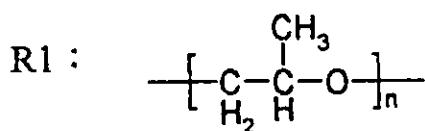
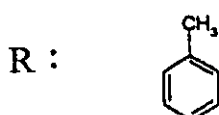
In general, the adhesion of dye to the fiber by means of vander waals force or electrostatic force is not strong enough. According to our previous study <sup>(8,9)</sup> on colored polyurethane ionomers, the reaction of diisocyanate with reactive dye in the presence of other additives to form dye-based polyurethane ionomers <sup>(1-7)</sup> with more hydrophilic groups may have better adhesion to the fiber. Owing to the environmental protection becoming increasingly important the organic solvent used as a diluent for synthetic resin has gradually been replaced by water. Therefore, the development of photosensitive-fluorescein polyurethane ionomer becomes important at present or in the future. Since the information on photosensitive-fluorescein polyurethane ionomers was not reported in the literature, therefore, we attempted to develop a unique way to prepare these ionomers and to further explore their physical properties. The reaction of toluene diisocyanate with fluorescein and other additives to form the possible structure of photosensitive-fluorescein polyurethane ionomer is given as follows:

+ Acetone  
 (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N  
 + Triethylamine  
 (TEA)



Water

photosensitive-fluorescein PU ionomer



- 
- 1) Correspondence to D. Y. Chao, Institute of Applied Chemistry, Chinese Culture University, Hwa Kang, Yang Ming Shan, Taipei, Taiwan
  - 2) C. P. Chwang and S. N. Lee, Department of Chemistry, FuJen University, Taipei, Taiwan

This paper was presented at the 10<sup>th</sup> International Symposium on Fine Chemistry and Functional Polymers (FCF-P-X), Shandong Normal University, China on 20-23 September 2000.

## Experimental

### Materials

Dimethylpropionic acid was purchased from Alcolac Industrial Chemical Co. (USA). N,N-dimethyl acetamide and triethylamine were received from Riedel-de Haen Co. (Germany). Polypropylene glycol (PPG) with molecular weight of 2000 and 700 was obtained from Chiunglong Petrochemical Co. Fluorescein and hydroxypropyl acrylate were supplied by Lancaster Co. (England) and Aldrich Chemical Co. Inc (USA), respectively. Toluene diisocyanate was purchased from Merck Co. (Germany). All of these materials were used without further purification.

### Method

A 0.03 equivalent of dimethylol propionic acid, 0.05 and 0.04 equivalent of respective polypropylene glycol (PPG) with molecular weight of 2000 and 700, 0.01-0.03 equivalent of hydroxypropyl acrylate, and 0.005-0.003 equivalent of fluorescein were charged to a 500 ml four-neck reaction kettle equipped with a stirrer, thermometer, and condenser, in the presence of 20g of N,N-dimethyl acetamide. The mixture was agitated at a speed of 500 rpm, and 0.156 equivalent of toluene diisocyanate was slowly added and then reacted in the presence of 0.2% (by weight) dibutyltin dilaurate at around 82°C for about 1.5 hr. To the solution containing 65g of acetone, 0.03 equivalent of

triethylamine was added to form a quaternized NCO-terminated polyurethane (PU) prepolymer. This quaternized prepolymer was further reacted with 170g of water in the presence of a small amount of diethylene triamine to form the photosensitive-fluorescein PU ionomer. After the acetone was completely removed from the photosensitive-fluorescein PU ionomer liquids by an evaporation technique, this ionomer product had an approximately 34% solid content. In aqueous solution, the surface tension, the viscosity and the number average particle sizes of these photosensitive-fluorescein PU ionomer molecules were fully investigated using a FACE surface tensiometer (CBVP-A3 type, Kyowa Interface Science Co. Japan), a brookfield digital viscometer (USA) and a dynamic light scattering spectrophotometer (47000, Malvern), respectively, at room temperature. In aqueous solution, the photosensitive-fluorescein PU ionomer with 34% solid content in the presence of benzoin or benzophenone was poured into a polypropylene dish to form a 0.2-0.3 mm dry film for tensile testing by Instron (GT-7010-A2, Gotech Testing Machines Inc, Taiwan). The experimental error for the measurements of these ionomers was estimated to be within  $\pm 0.5$ .

### **Results and discussions**

The IR spectra for toluene diisocyanate, hydroxypropyl acrylate and fluorescein are given in Figures 1,2 and 3, respectively. The NCO

functional group of TDI will rapidly react with polypropylene glycol, fluorescein, hydroxypropyl acrylate and other additives to form photosensitive-fluorescein, NCO-terminated polyurethane prepolymer. This prepolymer, given in Figure 4, is demonstrated by the formation of the absorbance peaks at around  $1537\text{cm}^{-1}$  (NHCO),  $3340\text{cm}^{-1}$  (NH),  $1720\text{cm}^{-1}$  (C=O),  $1633\text{cm}^{-1}$  (RCH=CH<sub>2</sub>),  $1451\text{cm}^{-1}$  (CH<sub>2</sub>-O-CO-), and  $1016\text{cm}^{-1}$  (C-O) and by almost the disappearance of the absorbance peak at around  $2275\text{cm}^{-1}$  (NCO). In comparison of Figures 1-3, these results suggest that the reaction of TDI with hydroxypropyl acrylate, fluorescein, dimethylol propionic acid and other additive does, in deed, form a photosensitive-fluorescein polyurethane ionomer. To further study the fluorescence for a dilute concentration of photosensitive-fluorescein polyurethane ionomer in aqueous solution by using fluorescence spectrophotometer (F-4500, Hitach, Japan), it exhibited fluorescence at around 508 nm, given in Figure 5. For a dilute concentration of photosensitive-fluorescein polyurethane ionomer in aqueous solution, the plots of the number average particle size versus the respective concentration of hydroxypropyl acrylate, fluorescein, and epoxy, at  $25 \pm 0.05^\circ\text{C}$ , are given in Figure 6. Figure 6 clearly indicates that the number average particle size is seen to increase appreciably with increasing concentration of hydroxypropyl acrylate, fluorescein and epoxy,



respectively, used to prepare the photosensitive-fluorescein PU ionomer molecule. This is the result of strong intermolecular interaction between ionomer molecules which may increase the free volume of these ionomer molecules, thus causing the number average particle size of ionomer molecule to increase. Similarly, the number average particle size versus the concentration of benzoin, given in Figure 7, is seen to increase with an increase in the concentration of benzoin. The explanation for this behavior is the same as described in Figure 7. All samples of photosensitive-fluorescein PU ionomer in aqueous solution with 0.25wt%-5.0wt% benzoin were irradiated from one side under a nitrogen atmosphere using a bank of 80-w mercury lamps ( $\lambda=365\text{nm}$ ) as the irradiation source. These samples after UV curing (150-453second) were dried in a vacuum oven at 50-60°C for at least 7h to remove water and unreacted reactive diluents. In aqueous solution, the UV irradiation time for photosensitive-fluorescein PU ionomer with benzophenone or benzoin in a fixed concentration of hydroxypropyl acrylate, given in Figure 8, appears to decrease with increasing concentration of benzophenone or benzoin. Experimentally, the photoinitiator such as benzophenone or benzoin at high concentration may force the C=C double bond of photosensitive-fluorescein PU ionomer molecule to quickly form free radicals in which the

polymerization or crosslinking immediately occurs. As believed, the samples cured completely by UV irradiation are likely to take place at high concentration of photoinitiator. In analysis of the experimental results shown in Figure 8, benzoin is better than benzophenone as a photoinitiator for the photosensitive-fluorescein PU ionomer molecule in terms of the UV irradiation time. As expected, the UV irradiation time is seen to gradually decrease with increasing concentration of hydroxypropyl acrylate used to prepare the photosensitive-fluorescein PU ionomer molecule, given in Figure 9. Under UV irradiation, the hydroxypropyl acrylate at high concentration is believed to form free radicals quickly. The chain propagation or crosslinking of these free radicals at high concentration of hydroxypropyl acrylate does, indeed, take place at short time of UV irradiation. A 0.2-0.3mm self-cured film of photosensitive-fluorescein PU ionomer molecule (under UV irradiation and dried in vacuum oven at 50-60 °C) was used for tensile testing by Instron, and the experimental results are given in Figures 10 and 11. The experimental results illustrate that the tensile strength appears to increase with increasing concentration of epoxy, fluorescein, hydroxypropyl acrylate and benzoin, respectively, as a result of strong intermolecular interaction resulting from increased hydrophilic groups of photosensitive-fluorescein PU ionomer molecule. In Figure 10,

the tensile strength stronger for PU ionomer molecule with epoxy than for PU ionomer molecule with fluorescein or hydroxypropyl acrylate may be attributed to strong intermolecular interaction due to increased hydrophilic groups attached to the backbone of PU ionomer molecule. More interestingly, increased concentration of benzoin in photosensitive-fluorescein PU ionomer molecules, shown in Figure 11, gives an increase in tensile strength. This may be due to enhance the polymerization between free radicals and C=C double bonds and crosslinking between hydrophilic groups of the photosensitive-fluorescein PU ionomer molecules in the presence of benzoin as a photoinitiator.

## Conclusion

We have successfully synthesized the photosensitive-fluorescein PU ionomer molecules at our lab, and their structures have been proven by IR spectra. The fluorescence study of a dilute concentration of photosensitive-fluorescein PU ionomer molecule in aqueous solution exhibits fluorescence at around 508nm. In aqueous solution, the number average particle size appears to increase with increasing respective concentration of epoxy, fluorescein and hydroxypropyl acrylate used to prepare photosensitive-fluorescein polyurethane ionomer molecule. This is the result of increased free volume of photosensitive-fluorescein PU ionomer molecule due to strong intermolecular interaction between ionomer molecules. It was found that the addition of a photoinitiator such as benzoin to the photosensitive-fluorescein PU ionomer molecule in aqueous solution results in increasing the average particle size of this ionomer molecule. To further study the relationship between the UV irradiation and the curing of photosensitive-fluorescein PU ionomer molecule, it has been found that the benzoin is better than the benzophenone as a photoinitiator for this PU ionomer system in terms of short time of UV irradiation. In addition, under UV

irradiation, the hydroxypropyl acrylate at high concentration, due to increased free radicals formed, is expected to have better performance of polymerization and/or crosslinking for photosensitive-fluorescein PU ionomer molecule. For self-cured films made by photosensitive-fluorescein PU ionomer molecule, the tensile strength appears to increase with increasing concentration of epoxy, fluorescein and hydroxypropyl acrylate, respectively. This is the result of increased crosslinking due to strong intermolecular interaction between hydrophilic groups of photosensitive-fluorescein PU ionomer molecule.

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## Acknowledgement

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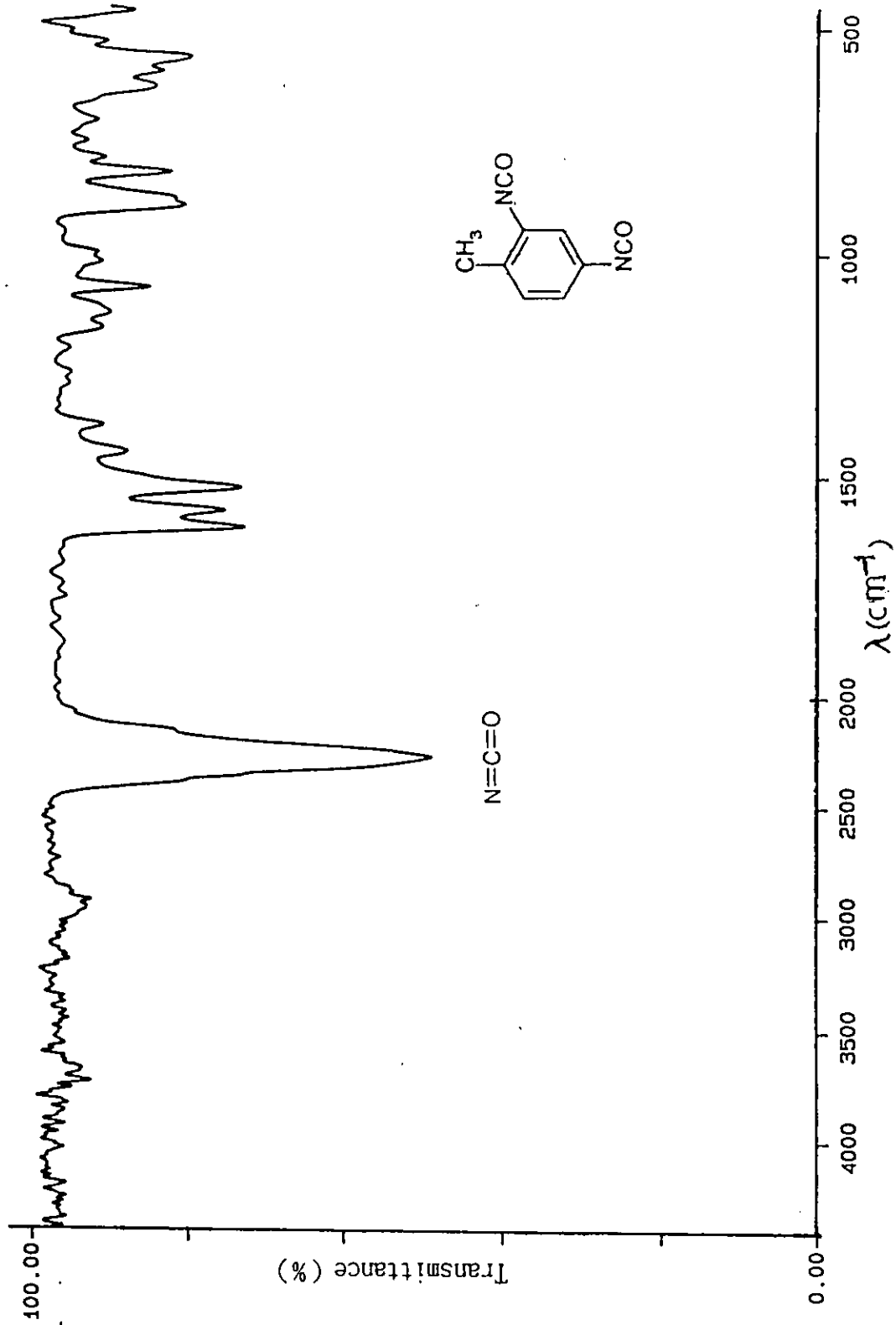


Figure 1 Spectra of toluene diisocyanate at  $25 \pm 0.05^\circ\text{C}$ .



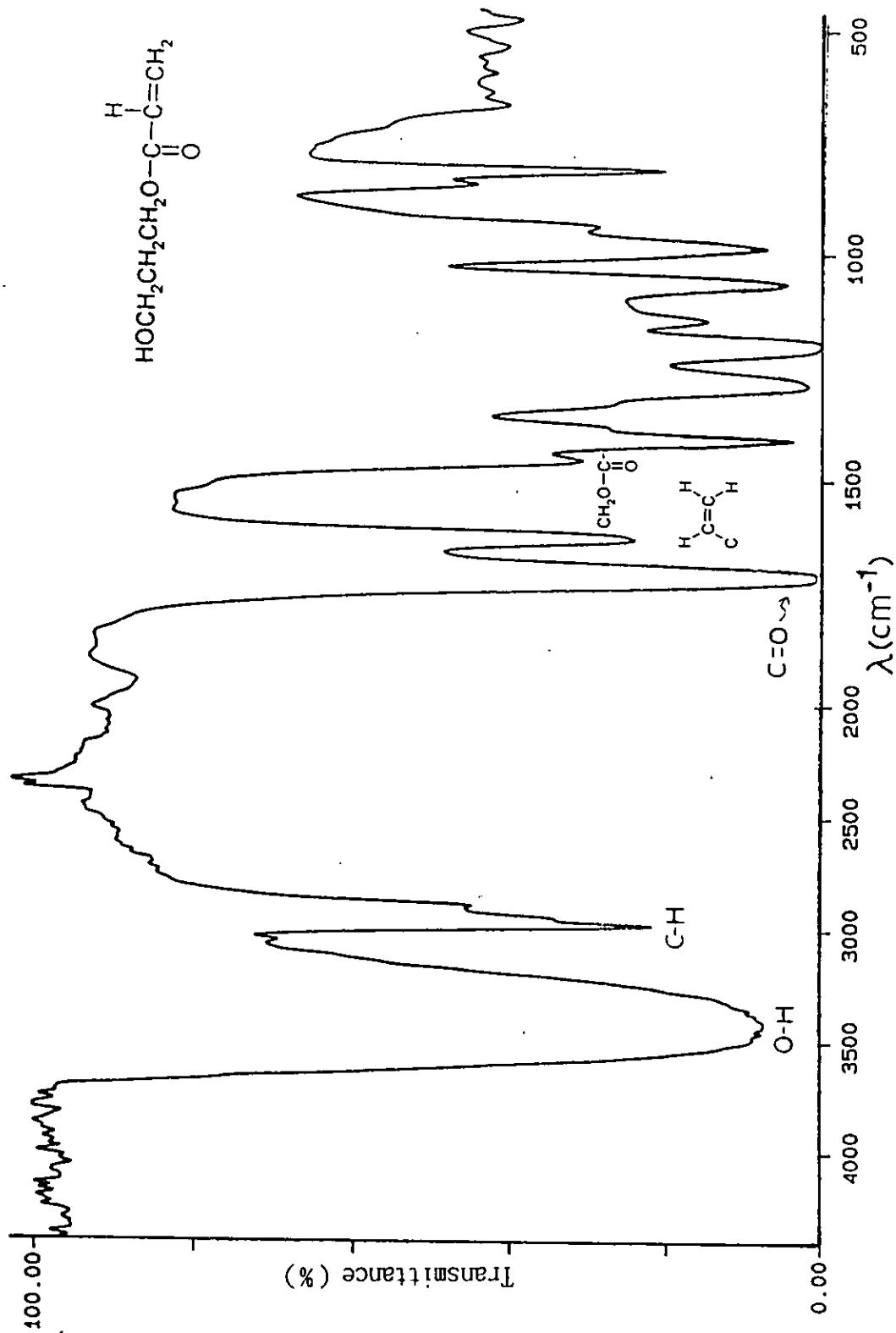


Figure 2 Spectra of hydroxypropyl acrylate at  $25 \pm 0.05^\circ\text{C}$ .

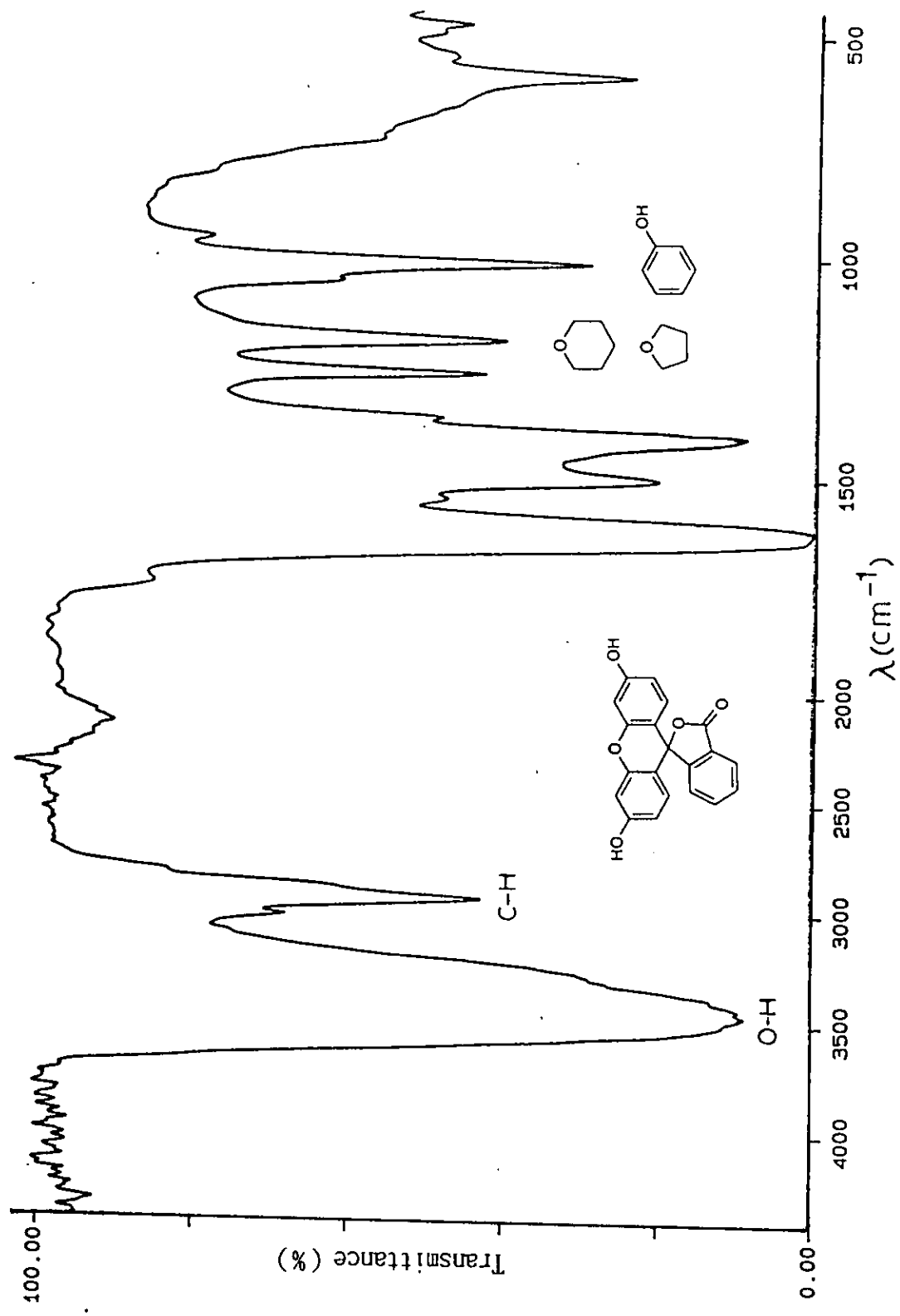


Figure 3 Spectra of fluorescein at 25±0.05°C.

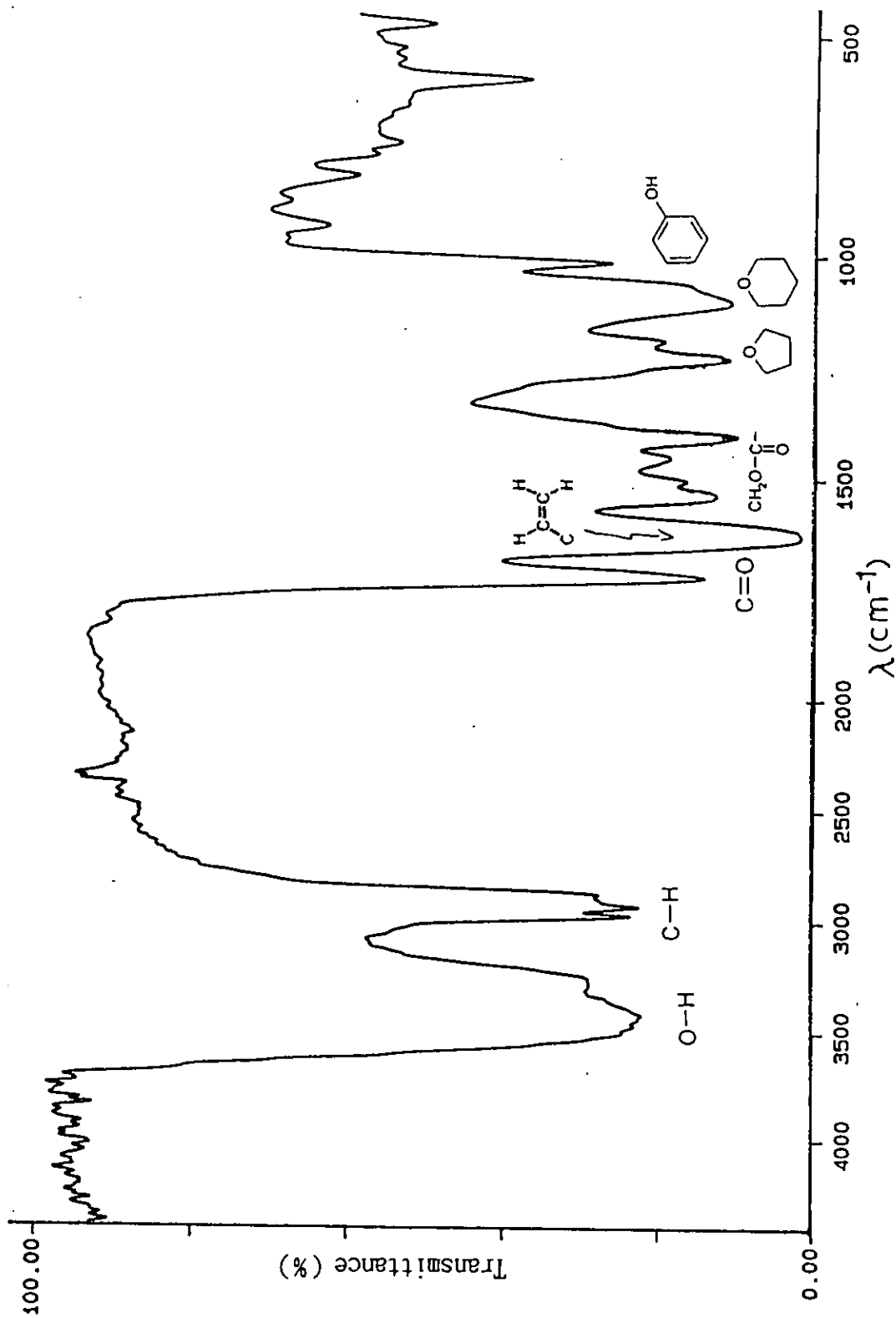


Figure 4 Spectra of photosensitive-fluorescein PU prepolymer formed after 2h reaction, at  $25 \pm 0.05^\circ\text{C}$ .

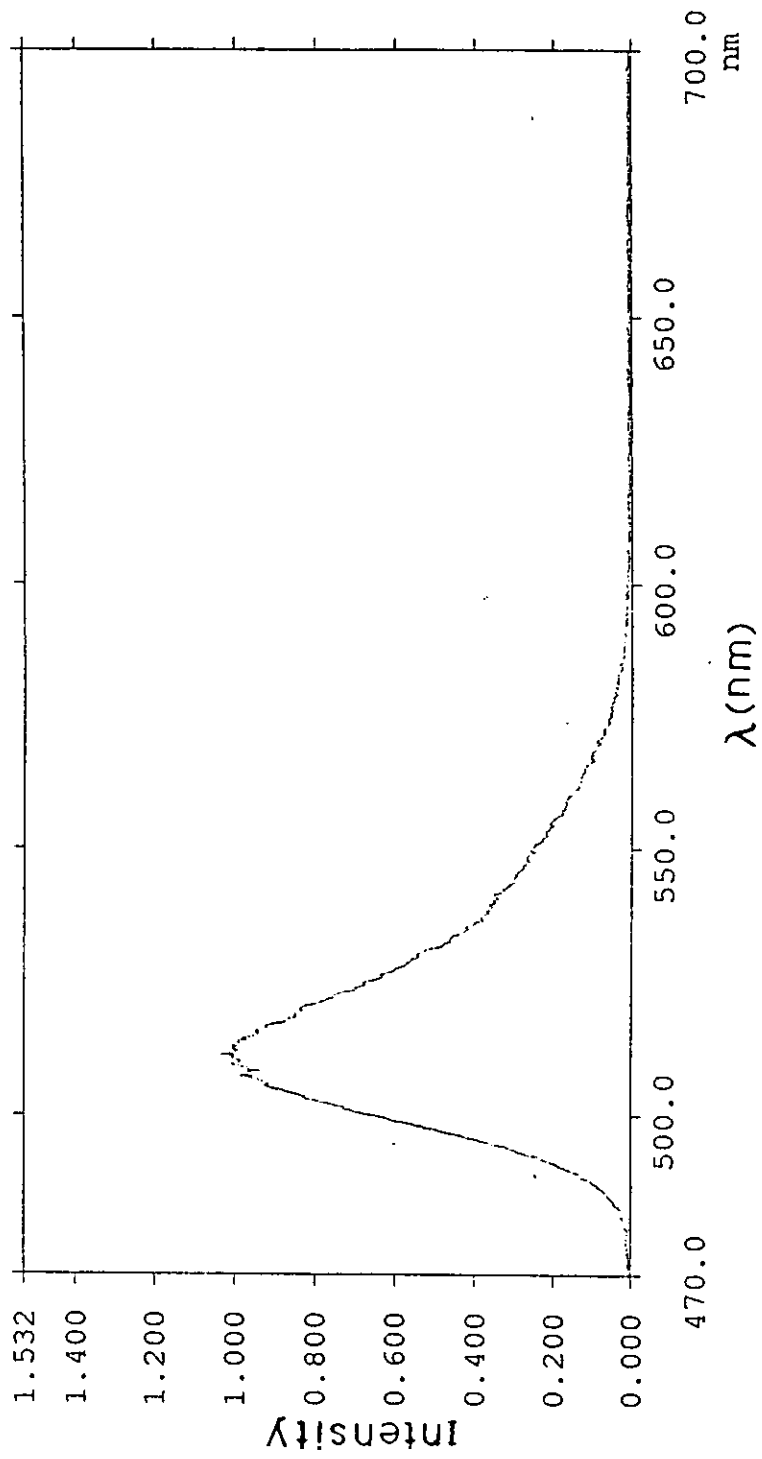


Figure 5 Fluorescence spectrum of photosensitive-fluorescein PU ionomer , at  $25 \pm 0.05^\circ\text{C}$ .

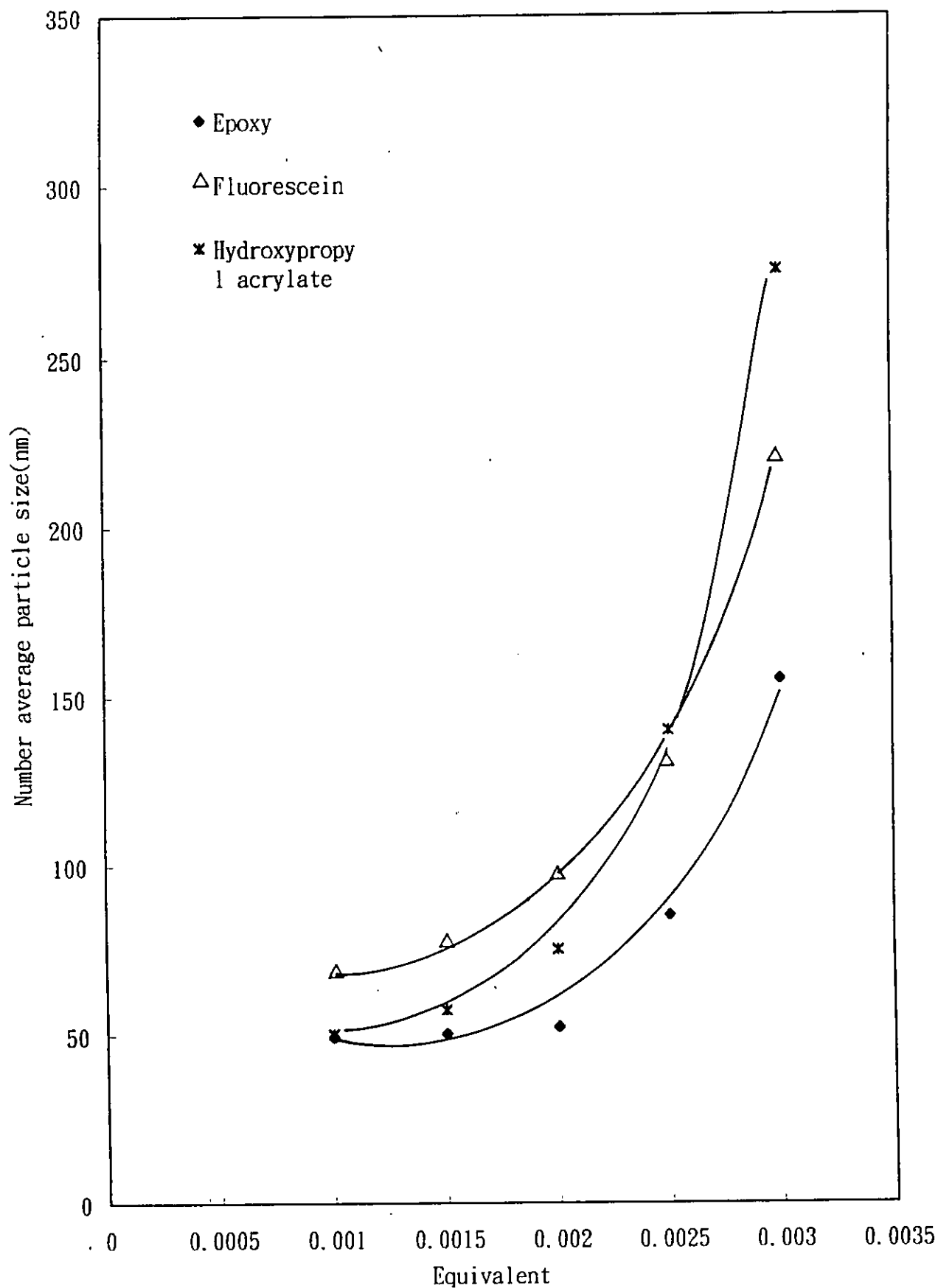


Fig6 Number average particle size versus the respective concentration of epoxy, fluorescein and hydroxypropyl acrylate used to prepare photosensitive-fluorescein polyurethane ionomer, at  $25 \pm 0.05^\circ\text{C}$ .

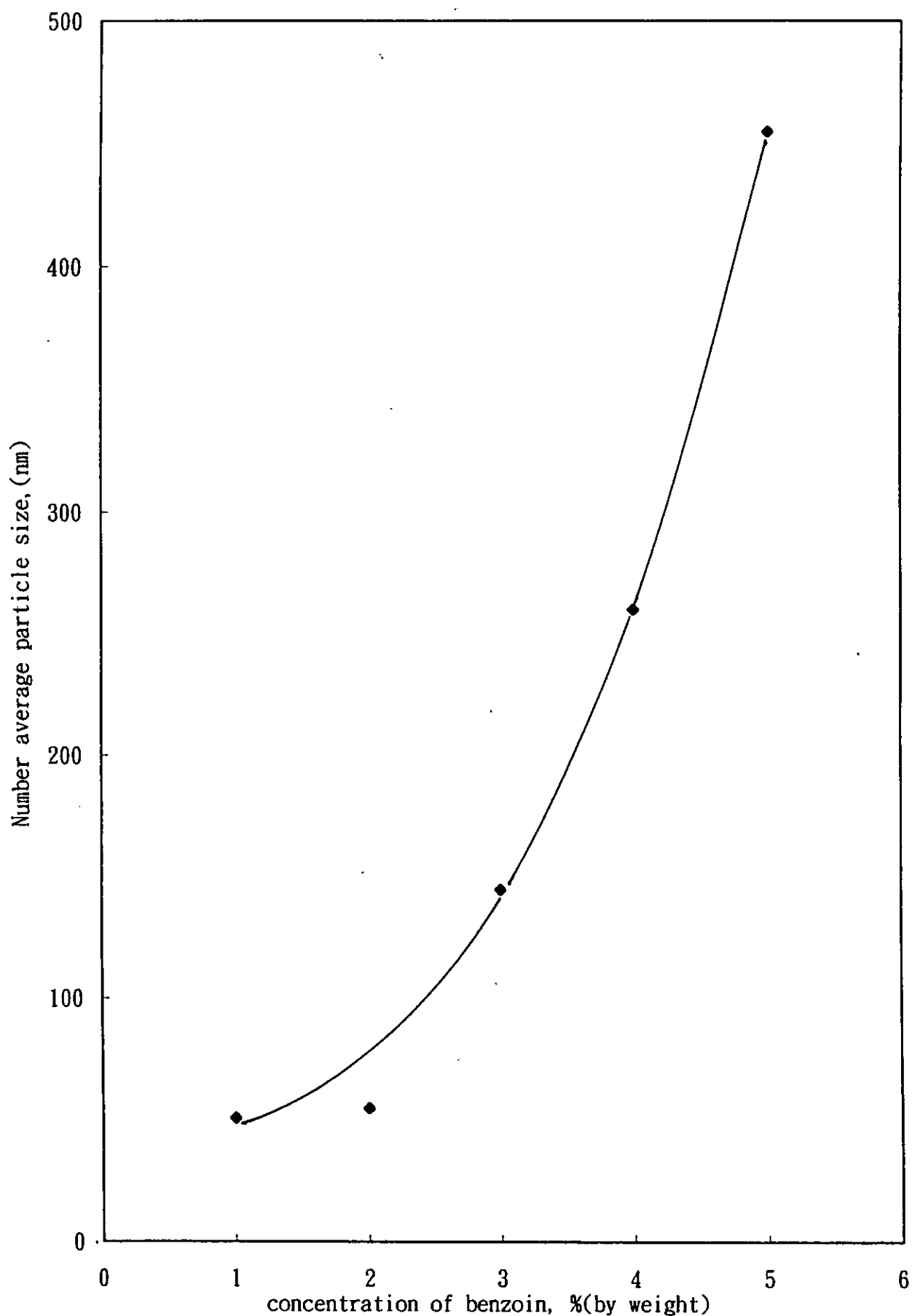


Fig7 Number average particle size versus the concentration of benzoin used to prepare photosensitive-fluorescein polyurethane ionomer, at  $25 \pm 0.05^\circ\text{C}$ .