



SYNTHESIS OF PHOTOCONDUCTIVE POLYMER OF POLY(4-DIPHENYLAMINO STYRENE) FOR PHOTOREFRACTIVE MATERIALS

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ABSTRACT

The typical synthesis procedure for the monomer of *N,N*-diphenyl-4-vinylaniline was conducted and has been proved to be ineffective in the university laboratory conditions. The modified procedure was applied successfully using freshly formed Wittig reagent. The monomer was characterized by proton nuclear magnetic resonance (¹H NMR) spectroscopy and confirmed the chemical structure with the correct peaks. The photoconductive polymer of poly((4-diphenylamino styrene)) could be obtained only by using the white crystal monomer.

Keywords: Wittig reaction, triphenylamine, synthesis, photoconductive polymer.

TÓM TẮT

Tổng hợp polymer quang dẫn poly(4-diphenylamino styrene) cho vật liệu quang phi tuyến

Phương pháp truyền thống để tổng hợp monomer *N,N*-diphenyl-4-vinylaniline đã được tiến hành và chứng minh là không hiệu quả trong điều kiện phòng thí nghiệm. Quy trình cải tiến đã được áp dụng thành công sử dụng tác nhân Wittig vừa được hình thành. Cấu trúc hóa học của monomer được phân tích bằng phổ cộng hưởng từ hạt nhân proton và xác nhận sản phẩm với các đỉnh đặc trưng. Polymer quang dẫn poly((4-diphenylamino styrene)) chỉ có thể được tổng hợp với monomer tinh thể màu trắng.

Từ khóa: phản ứng Wittig, Triphenylamine, tổng hợp, Polymer quang dẫn.

1. Introduction

Photorefractive (PR) polymer composite has been extensively researched in the recent years owing to its updatable holographic property.[1, 2] Updatable three-dimensional (3D) display technology has been demonstrated using PR composites.[3-5] Typical components for PR composite include a photoconductive polymer, a nonlinear optical chromophore, a plasticizer and a sensitizer. The polymer plays an important role in providing a charge transport media and the dispersive matrix for the other components. Triphenylamine moiety has been utilized as the charge transport agent for PR polymers

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owing to its fast hole mobility.[6, 7] The triphenylamine acrylate type and triphenylamine styrene type polymers have been reported to have a fast response by Tsujimura et al.[8] The triphenylamine polymer was also applied to other organic electronic and photonic devices such as solar cells, OLED...[9]. The response of the composite also depends on the method of the synthesis as well as the purity of the polymer. In this study, we investigate the synthesis of styrene type photoconductive polymer: poly((4-diphenylamino styrene)). The published synthesis procedure[10] has been proved to be insufficient for the monomer of N,N-diphenyl-4-vinylaniline (DAS). A new procedure comparing to the previous study is performed utilizing the freshly formed Wittig reagent.

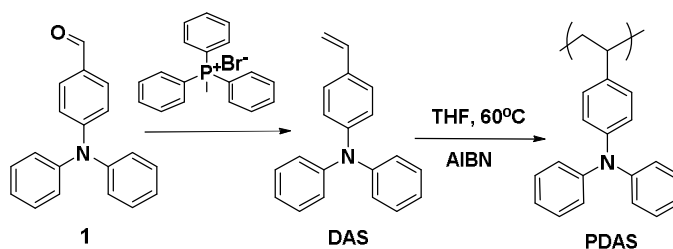
Many controlled polymerization techniques have been developed and applied to synthesizing organic semiconductor polymers.[11, 12] However, these methods include several catalysts and additional compounds which might be difficult to be removed after forming the polymer. Therefore, instead of using living or controlled polymerization method, the simple free radical polymerization with very low concentration of initiator is applied. The effect of monomer impurity to the polymerization process is also conducted and compared.

2. Experimental Section

2.1. Materials

4-(Diphenylamino)benzaldehyde was purchased from Wako (Japan). Azobisisobutyronitrile (AIBN) was product of Sigma-Aldrich. Methyl triphenylphosphonium-bromide and potassium-*tert*-butoxide were obtained from Aladdin company (Shanghai-China). Tetrahydrofuran (THF) is the pure type for chromatography and is the product of Merck (Germany). The other chemicals were purchased from Xilong company (China).

2.2. Synthesis



Scheme 1. Synthetic route for poly((4-diphenylamino styrene))

In this study, poly((4-diphenylamino styrene)) (PDAS) was synthesized following the synthetic route shown in Scheme 1. Firstly, the DAS monomer was synthesized using Wittig reaction with methyl triphenylamine phosphonium bromide. Then, by using free-radical polymerization method, the obtained monomer was added with initiator of AIBN in a solution to form the corresponding polymer of PDAS.

2.3. Synthesis of *N,N*-diphenyl-4-vinylaniline (DAS)

Two different procedures have been applied to synthesize the monomer. The first one was set up according to the literature[10] and was described as following:

Methyl triphenyl-phosphonium-bromide (1 g, 2.8 mmol) is suspended in 25 mL THF under nitrogen gas. The temperature was reduced to 0 °C by a bath of ice and water. Potassium-*tert*-butoxide with different mole ratios to aldehyde (**1**) was added. 4-(diphenylamino)benzaldehyde (**1**) (0.5 g, 1.83 mmol) was added drop-wise at 0 °C. All the processes were conducted under the continuous nitrogen gas. Then, the mixture was sealed and warmed up to room temperature and left stirring overnight.

The second procedure is as below:

4-(diphenylamino)benzaldehyde (**1**) (2 g, 7.32 mmol) and methyl triphenyl-phosphonium-bromide (3.14 g, 8.78 mmol) was dissolved in THF (25 mL). Then, the potassium-*tert*-butoxide (1.2 g, 11mmol) was added. The solution was left stirring overnight.

In both cases, the reaction was monitored by thin layer chromatography (TLC) with ethyl acetate: hexane (1:3 or 1:6) as the eluent. At the end of reaction, 20 mL of deionized water was added. The solution was extracted with dichloromethane. The organic layer was dried over K₂CO₃ and the solvent was removed by rotary evaporator. The crude product was purified by column chromatography with silica gel. All of the solutions which contain the substance at the same desired R_f were collected. The solvent was removed by rotary evaporator to receive the final product.

2.4. Synthesis of poly((4-diphenylamino styrene)) (PDAS)

A mixture of DAS monomer (1 g, 3.68 mmol) and AIBN initiator (0.6 mg, 0.036 mmol), THF (1 ml) was degased carefully (3 times). The mixture was heat up to 60 °C by an oil bath. After 20 hours, the mixture was diluted with THF (14 ml) and then precipitated into methanol (200 ml). The obtained precipitation was collected by vacuum filtration. The solid was dried in an oven at 60 °C for 24 h to obtain the final polymer powder. The yield of reaction was calculated based on the ratio of weight of collected polymer powder and original monomer.

3. Results and Discussion

The TLC results with ethyl acetate : Hexane (1:3) were shown in Figure 1. The left spot is 4-(Diphenylamino)benzaldehyde while the right spot is the reacted solution. Figure 1 a, b and c are the results using different amount of base. The mole ratios of 4-(Diphenylamino)benzaldehyde / methyltriphenylphosphonium-bromide / potassium-*tert*-butoxide are 1/1.5/1.5, 1/1.5/2 and 1/1.5/4 for Figure 1 a, b and c, respectively. As can be seen, following the first procedure, the TLC spot of 4-(Diphenylamino)benzaldehyde was remained and the product spot could not be observed.

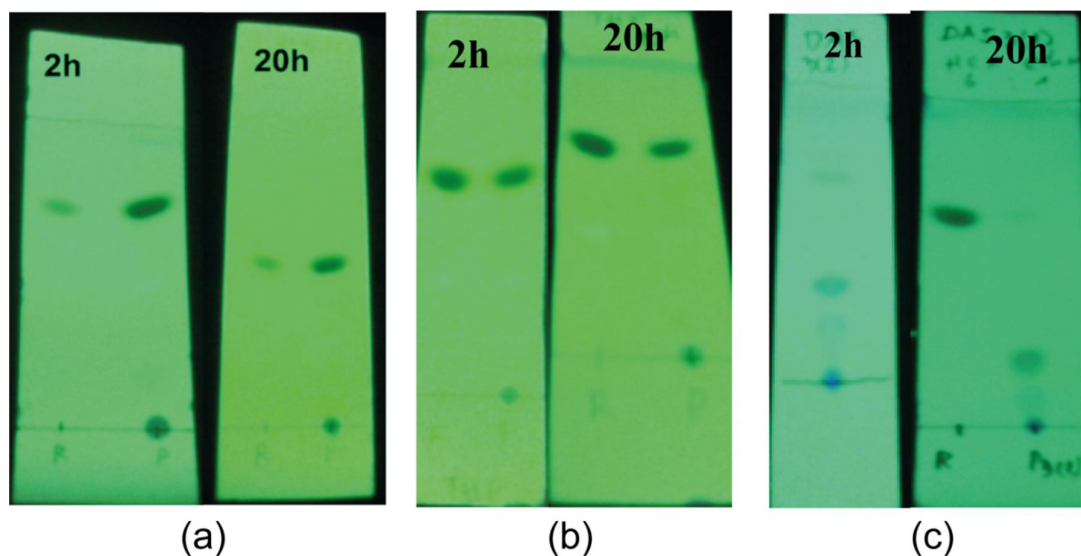


Figure 1. Thin layer chromatography (TLC) of monomer synthesis reaction. Mole ratio of 4-(Diphenylamino)benzaldehyde/methyltriphenylphosphonium bromide/potassium *tert*-butoxide: a) 1/1.5/1.5; b) 1/1.5/2; c) 1/1.5/4

The result indicates that the reaction was not occurred even after 20h. When the used amount of potassium-*tert*-butoxide was increased up to 4 equiv., the spot of aldehyde reagent was disappeared. The other spot which has a lower R_f appeared. The compound was isolated by column chromatography and the structure was investigated by $^1\text{H-NMR}$. However, from the NMR result, we have confirmed that the isolated compound is not the desired monomer.

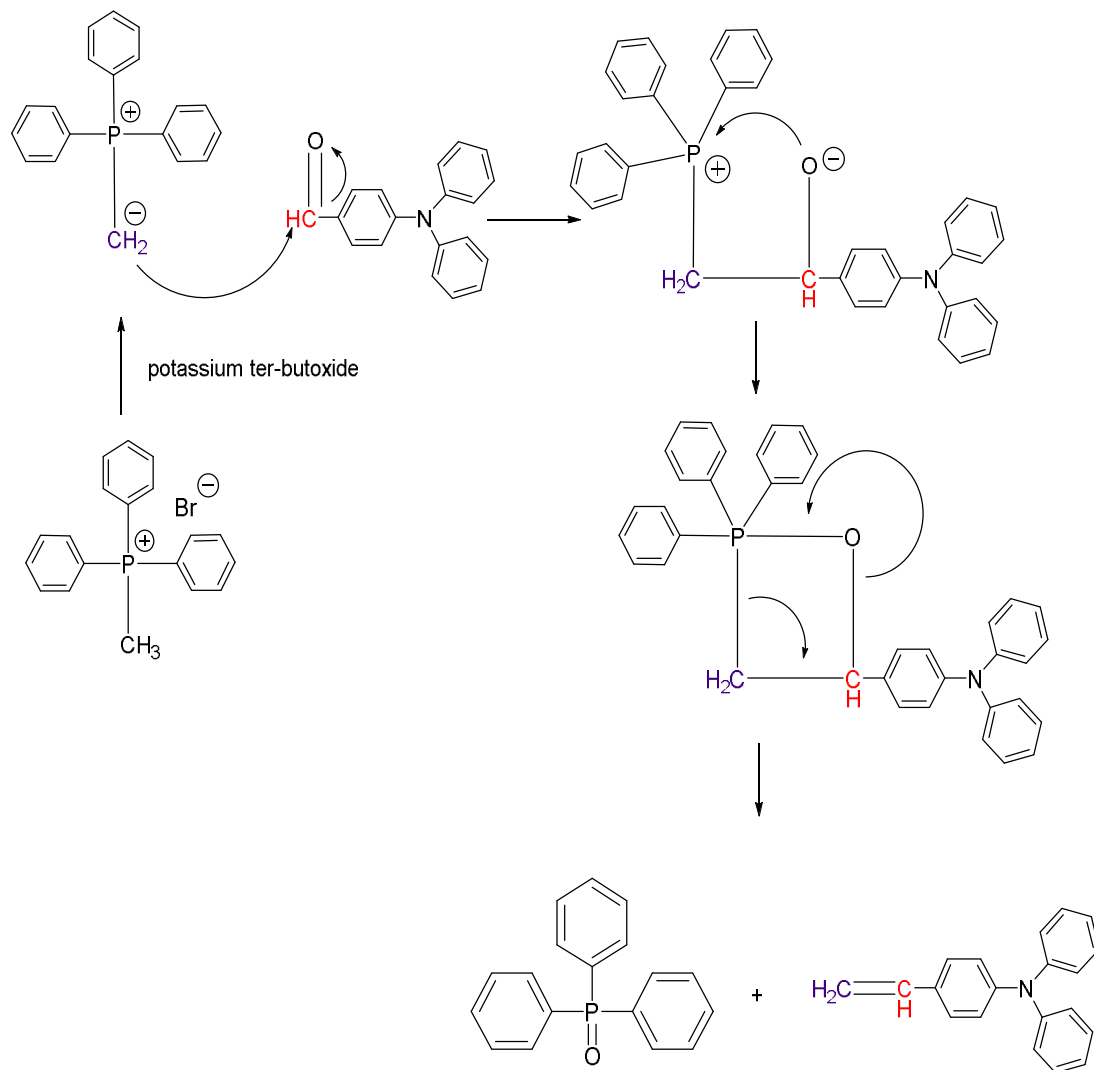


Figure 2. Mechanism of Wittig reaction for monomer DAS

The first procedure (experimental section) for synthesis of monomer was designed according to the Wittig reaction mechanism. The mechanism is summarized in Figure 2. Firstly, Wittig reagent was formed by the reaction between methyltriphenylphosphonium bromide and a strong base which was potassium-*tert*-butoxide in this study. The Wittig reagent was then reacted with aldehyde group of 4-(Diphenylamino)benzaldehyde to form the corresponding styrene type monomer. The purpose of this procedure is to form Wittig reagent by mixing methyltriphenylphosphonium bromide and potassium-*tert*-butoxide prior to addition of the aldehyde compound. After adding the base, the color of the solution was changed to yellow, indicating that the Wittig reagent had been formed. However, the

yellow color of the solution was quickly disappeared. The result suggested that the Wittig reagent has been consumed before the aldehyde compound was added. Degasing the solvent and the solution with nitrogen could only delay the process but the final result was inevitable. Although the reason for this phenomenon has not been made clear, the initial result could confirm that the disappearance of Wittig reagent was the main course. Therefore, the second procedure was designed in a different manner.

To avoid the consummation of Wittig reagent, methyltriphenylphosphonium-bromide and 4-(Diphenylamino)benzaldehyde were mixed in THF without the strong base. Potassium *tert*-butoxide was added later to the solution and Wittig reagent could be formed with the presence of aldehyde. By applying this method, the freshly created Wittig reagent will immediately react with aldehyde compound to form the corresponding monomer. The method is very effective as the TLC spot of the original benzaldehyde compound was faded gradually and nearly disappeared after 2 hour of reaction. Simultaneously, a new spot with higher R_f ($R_f = 0.8$, ethyl acetate : hexane (1:6)) was appeared. This product was isolated by column chromatography (silica gel) using the eluent of ethyl acetate : hexane (1:6). A yellow product was obtained with the $^1\text{H-NMR}$ result shown in Figure 3. There are 2 peaks at chemical shift of 5.179 and 5.661 ppm which represent *cis* and *trans* proton ((1) and (2)) in Figure 3. Each of the protons has spin-spin coupling with an adjacent proton by a coupling constant of 6.6 Hz and the resulted peak is doublet. Besides, due to the difference in *cis* and *trans* isomer, proton (1) and (2) also have a spin-spin coupling with a small splitting as can be observed in Figure 4. Proton (3) was spin-spin coupled from separated proton (*cis* and *trans*). Therefore, a quartet was observed with the same coupling constant of 6.6 Hz which is a clear evidence for the coupling. The calculated integration values also re-confirmed the assignment for each proton. The peaks above 7 ppm were assigned as the protons in the benzene ring. From the $^1\text{H-NMR}$ result, the desired monomer was confirmed. All of the other peaks represent for the solvents used in the purification processes including hexane, ethyl acetate and chloroform- d for $^1\text{H-NMR}$. The yellow color of the monomer is also in well agreement with the previous study.[10]

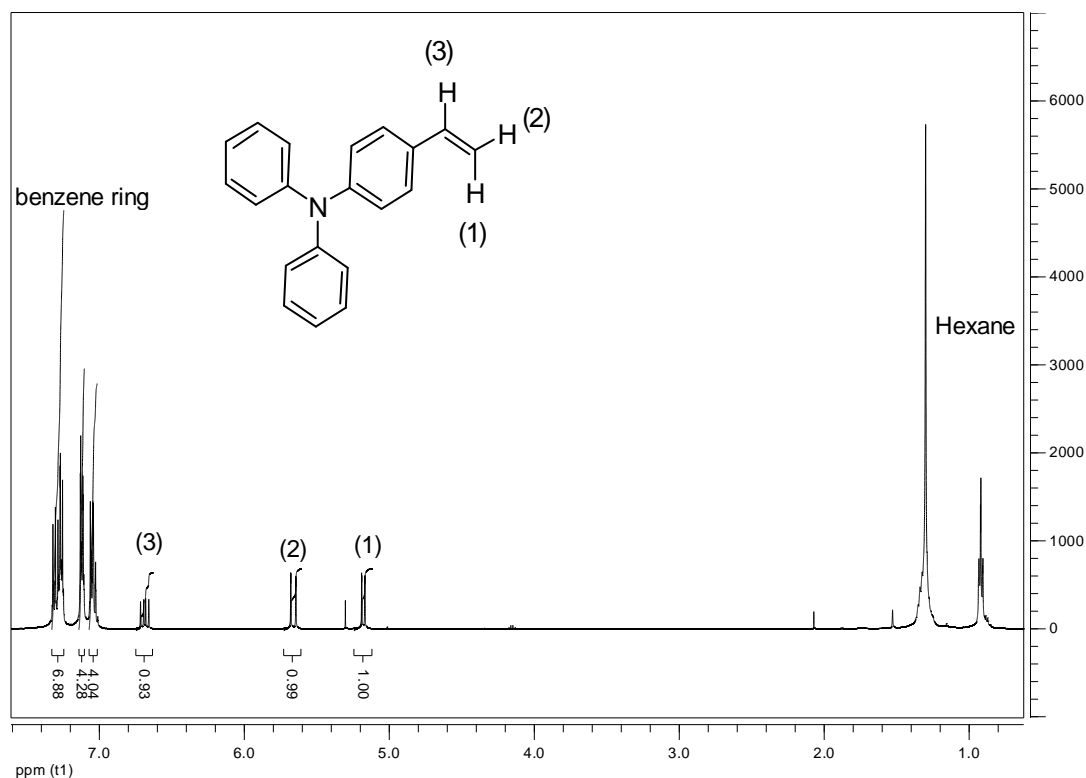


Figure 3. 300 MHz ^1H NMR of *N,N*-diphenyl-4-vinylaniline (CDCl_3 as the solvent)

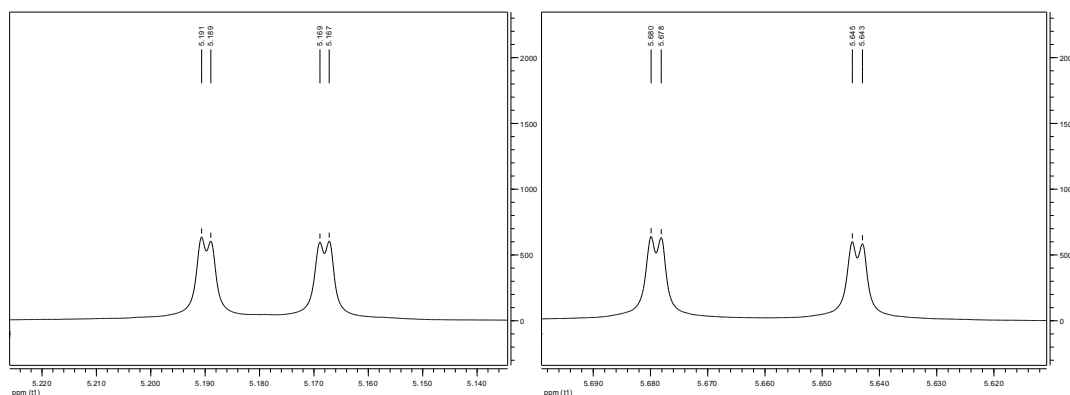


Figure 4. Enlarged ^1H NMR spectra in the vicinity of 5.18 ppm and 5.66 ppm

After successfully synthesizing of DAS, the obtained monomer was used for the next step, i.e. the polymerization process. As described in the experimental section, the procedure was conducted using freeze-pump-thaw method. In a Schlenk tube, the solution including monomer, initiator and solvent was completely frozen by liquid nitrogen and the reaction tube was opened to vacuum in at least 3 minutes. After sealing the tube, the

freezing solution was left melting at room temperature. The process was repeated 3 times to remove all of oxygen and water inside the reaction tube.

The first experiment was conducted with 1 g of the yellow monomer (0.1 % AIBN as an initiator) in 1 ml of THF. Although the reaction condition was strictly controlled, the polymer could not be formed after 24 hours. The reason might relate to the purity of the monomer. The monomer was again passed through the column chromatography. In this case, the less polar solvent (only hexane) was used as the eluent ($R_f = 0.5$). The solution after passing through the column is transparent and the obtained monomer is white crystal (Figure 5). The monomer in this study is considered to have a higher purity than the yellow product reported by Masanobu et al.[10]



Figure 5. Appearance of monomer *N,N*-diphenyl-4-vinylaniline (DAS) in a Schlenk tube

The second polymerization reaction was carried out applying the same condition with the white monomer crystal. After precipitation in methanol, a yellow powder of polymer was obtained and the reaction yield could achieve 39 %. As the amount of solvent (THF) was increased to 1.5 ml, the reaction yield was significantly reduced to less than 10 %. This phenomenon could be explained by the decrease of monomer and initiator concentration. The molecular weight of polymers for both experiments was characterized using gel permeation chromatography (GPC). The experiment was conducted on GPC equipment (SYSTEM-21, Shodex, Japan) using two columns KF805 and KF803 (Shodex Japan) with UV absorption detectors (at 250 nm). The GPC system was operated at a

typical condition (flow rate of 1 mL/min, temperature of 40 °C) and THF (HPLC grade, Wako Japan) was used as the eluent. The calibration was done using polystyrene ($M_w = 1.6 \times 10^3 \sim 3.2 \times 10^6$) as a standard. The GPC results were shown in Table 1. As can be seen, the weight average molecular weight (M_w) of PDAS can reach 54300 and polydispersity (M_w/M_n) is less than 2. However, as the solvent was increased, the molecular weight was decreased to 27300 and the polydispersity was larger than 2. The GPC result is also a clear evidence for the formation of polymer.

Table 1. Molecular weight of PDAS

Amount of solvent (mL)	M_w	M_n	M_w/M_n
1	54300	29500	1.84
1.5	27300	12700	2.15

4. Conclusions

The monomer of N, N-diphenyl-4-vinylaniline (DAS) and photoconductive polymer of PDAS were synthesized successfully. The procedure of Wittig reaction for the monomer has to be modified to obtain the product. 4-(Diphenylamino)benzaldehyde and methyltriphenylphosphonium bromide were firstly mixed and the potassium-tert-butoxide was added later. The yield of the reaction could achieve 30 %. The crude monomer was purified by column chromatography with hexane to obtain white monomer crystal. The yellow crystal monomer could not be used for polymerization while 39 % yield polymerization could be achieved with the white monomer crystal. The molecular weight $M_w = 54300$, $M_n = 29500$ and polydispersity of 1.84 could be achieved. Increasing the amount of solvent in polymerization will significantly reduce the yield of polymerization reaction.

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