Chemistry

NEW MONOMERS FOR CHEMICAL VAPOR DEPOSITION POLYMERIZATION OF POLY(P-XYLYLENE)

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Abstract. It was demonstrated that Poly(p-Xylylene) (PPX) could be prepared from α,α'-Bis(Alkoxy or Aryloxy) –p-Xylenes via chemical vapor decomposition (CVD)-method. This is one-step process and there are side products by the CVD-process. This effect depends both on the CVD- condition and the properties of the starting monomer. The structure and thermal behavior of the material were characterized by FTIR, UV-vis spectroscopy, elemental analysis, wide-angle X-ray diffraction, DTA and DSC. It could be showed that the deposited PPX is semicrystalline and the melting process of PPX is characterized by the two crystalline phase transition and accompanied by decomposition. This research will open a new way to synthesize of PPX.

1. INTRODUCTION

Poly(p-xylynene) (PPX) and its derivatives have potential as interlayer dielectrics because of their high thermal and chemical stability, excellent mechanical properties, low dielectric constant, and the fact that they can be synthesized and processed as thin coatings by chemical vapor deposition (CVD) [1,2]. The advantage of CVD-material, in particular, is that the CVD film deposition is generally conformal, exhibits good gap-fill properties. The deposition process is also solventless, which minimizes chemical disposal cost. The first preparation of PPX -film via CVD was reported by Gorham [3]. Although Gorham process is the most popular method of PPX polymerization, but because of their limitation of the availability of paracyclophane and the vaporizability of substituted paracyclophane, many other synthetic route for PPX are developed [1, 4-7]. Fig. 1 shows the different polymerization schemes used for CVD of PPX thin film.

In this paper, we present a new polymerization scheme of PPX thin film via CVD method. As the starting material, the monomer based on the ether-compounds was used. The reaction mechanism by CVD-process was investigated and the influence of the CVD-condition on the deposited material was discussed. The structure and thermal behavior of the deposition material was characterized by FT-IR, UV-vis, elemental analysis, TGA, DSC and X-ray diffraction.
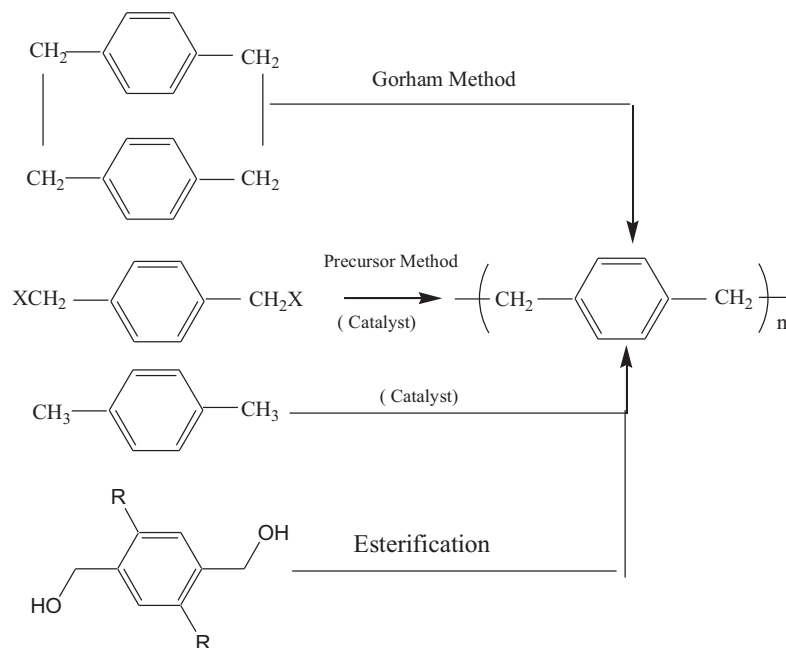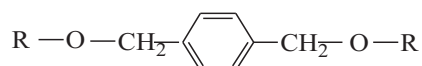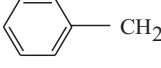
Fig. 1. Different synthesis techniques studied for PPX thin film deposition

2. EXPERIMENTAL SECTION

The used monomers for the investigation are listed on the Table 1.

Table 1. *The starting monomer for the investigation*

Monomer	Monomer 1 (liquid)	Monomer 2 (liquid)	Monomer 3 (solid)	Monomer 4 (solid)
R	CH_3	CH_3-CH_2		

The monomer 1 und monomer 2 are a commercially available products and was purchased by TCI and Sigmal-Aldrich company. The monomer was used without further purification. The monomer 3 and monomer 4 were synthesized in our Lab. Fig. 2 shows the synthesis routes for the monomer 3 and 4:

Monomer 3 and 4 are solid. They have a melting point of 144°C and 65°C determined by DSC with heating rate 10°C/min.

Fig. 3 shows the schematic experimental setup for CVD-process.

The CVD-process was performed by inert gas atmosphere with a steady flow rate of 8 mL/min and by pressure of 1 Torr. The monomer (0.5 ml for monomer 1 and 2, 80 mg for monomer 3 and 4) was placed on a tungsten boat

A

$$CH_2Cl\text{—}\langle\bigcirc\rangle\text{—}CH_2Cl \;+\; \langle\bigcirc\rangle\text{—}OH$$

Caltalyst $(CH_3(CH_3)_3)_4NBr$ K_2CO_3

Solvent CH_3CN T= 70 - 80°C

$$\langle\bigcirc\rangle\text{—}O\text{—}CH_2\text{—}\langle\bigcirc\rangle\text{—}CH_2\text{—}O\text{—}\langle\bigcirc\rangle$$

B

$$CH_2Cl\text{—}\langle\bigcirc\rangle\text{—}CH_2Cl \;+\; \langle\bigcirc\rangle\text{—}CH_2\text{—}OH$$

Caltalyst NaH

Solvent THF   T=50°C

$$\langle\bigcirc\rangle\text{—}CH_2\text{—}O\text{—}CH_2\text{—}\langle\bigcirc\rangle\text{—}CH_2\text{—}O\text{—}CH_2\text{—}\langle\bigcirc\rangle$$

Fig. 2. Synthesis route for monomer 3 (A) and monomer 4 (B)

Fig. 3. Schematic experimental setup for CVD-process

and vaporized by the temperature of 90-95°C (for monomer 1, 2 and 4) and 150-155°C for monomer 3. The vaporized monomer was allow to pass through the pyrolysis zone. The material deposited on the substrate and on the inner wall of the pyrolysis quartz tube in the deposition zone. For the IR-investigation, the sample was prepared on the KBr-pellet, for UV-vis investigation on the quartz substrate, for R-ray diffraction on the polycrystalline Si-wafer.

The IR-investigation was performed by the FTIR-BOMEM equipment, the UV-vis investigation by the HEWLETT PACKARD equipment. The elemental analysis was implemented by the Elemental Analyzer - Flash EA 1112 series/ CE instrument. The combustion temperature is 1100°C. The DTA and DSC-investigation was performed by Mettler-Toledo instrument TC15 and DSC821 under N_2-atmosphere. The heating and cooling rate is 10°C/min. For elemental analysis, TGA and DSC investigation, the material was collected on the inner wall of the pyrolysis quartz tube. The X-ray investigation was implemented by the RINT2000 Wide angle goniometer.

3. RESULTS AND DISCUSSION

Fig. 4 shows the IR-spectrum of the new material prepared by monomer 1 compared to the IR-spectrum of PPX.

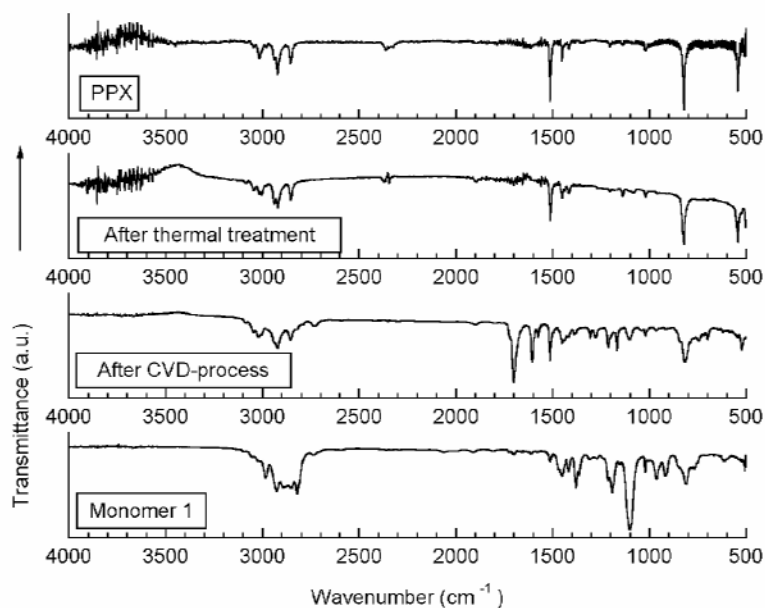**Fig. 4**. Comparison of IR-spectra of the new material and PPX

The material were prepared by the pyrolysis temperature $T_{CVD} = 800°C$ and by substrate temperature about $50°C$. PPX was prepared by Gorham-method with paracyclophane as starting material. Firstly it is to note that some liquids were observed on the substrate and in the deposition zone after the CVD-process. Obviously side products were formed during the CVD-process. To remove the side products, the sample was dried by the temperature of $200°C$ for 2h under vacuum. Comparison the IR-spectra of the sample before and after thermal treatment, it is clearly to see that the two strong absorption peak at 1701, 1609 cm^{-1} and some many absorption peak in the region from 1300 to 900 cm^{-1} are disappeared. This result indicates that the side products could be removed by thermal treatment. The spectrum of the new material after thermal treatment is completely different compared to the IR-spectrum of the monomer. The characteristic absorption peak of the monomer 1 is the absorption peak from C-O-C group at the wavenumber 1103 cm^{-1}. After CVD-process, this peak is disappeared by the new product. On the IR-spectrum of the new product, we can see the characteristic absorption peak from sp^2 C-H stretching ($3025\ cm^{-1}$), sp^3 C-H stretching (2942 to $2849\ cm^{-1}$), C=C ring stretching ($1518, 1456, 1425\ cm^{-1}$) and phenyl C-H bending ($823\ cm^{-1}$). Comparing the IR-spectrum of the new material and IR-spectrum of PPX, it is to note that both spectra are identical.

Fig. 5 shows the IR-spectra of the new materials prepared by monomer 2, 3 and 4. The pyrolysis temperature is 800°C.
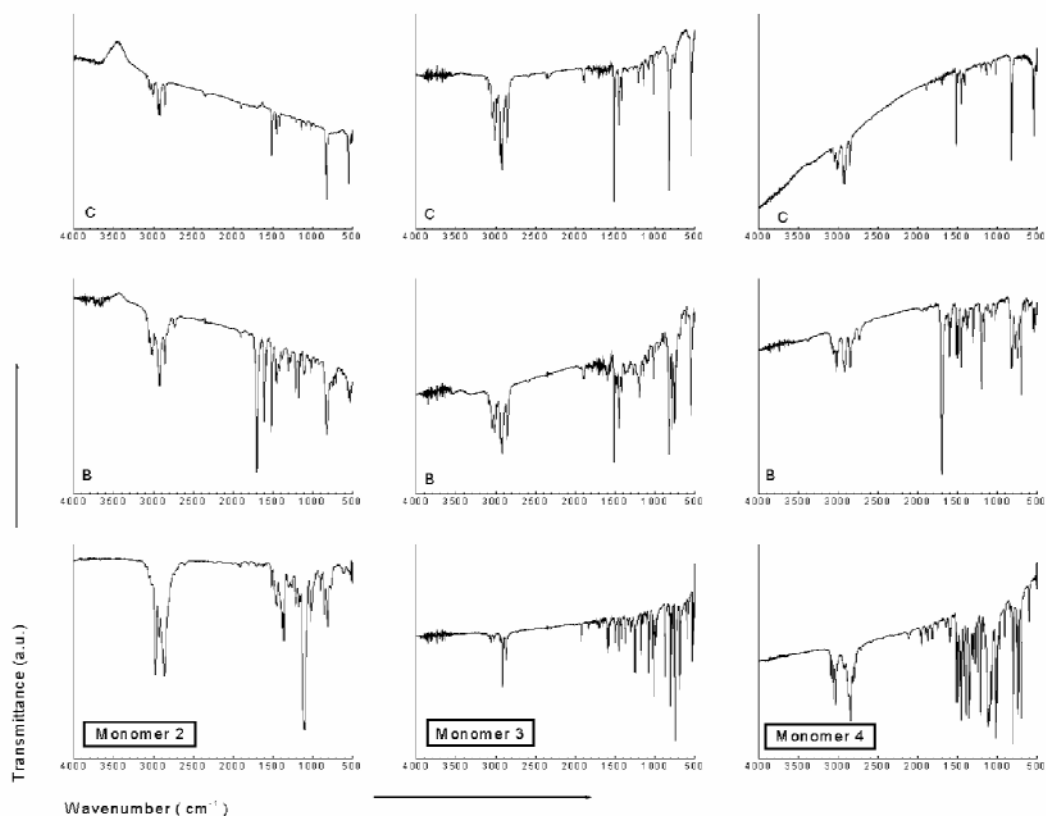

Fig. 5. IR-spectra of the new materials prepared by different monomers (B): After CVD-process, (C): After thermal tratment

It is necessary to remark that like monomer 1, the material prepared by monomer 2 by the substrate temperature of about 50°C could be recorded by IR-spectroscopy. But for monomer 3 and 4, the formed film were very thin by this substrate temperature so that it can not recorded by IR-spectroscopy. In the literature [8] is well known that the deposition rate depends on the substrate temperature and the colder the substrate temperature is, the thicker the deposited film is formed. For this reason, it was prepared by cold substrate temperature for monomer 3 and 4. The deposition zone was cooled by dry ice and the substrate temperature is about -10°C

Like the monomer 1, the new materials were strongly contaminated by the side products for all the 3 monomers after CVD-process. After thermal treatment, the IR-spectra of the materials are the same as the IR-spectrum of PPX.

To identify the new product, Fig. 6 shows again the UV-vis spectra of the new products prepared by 4 monomers.
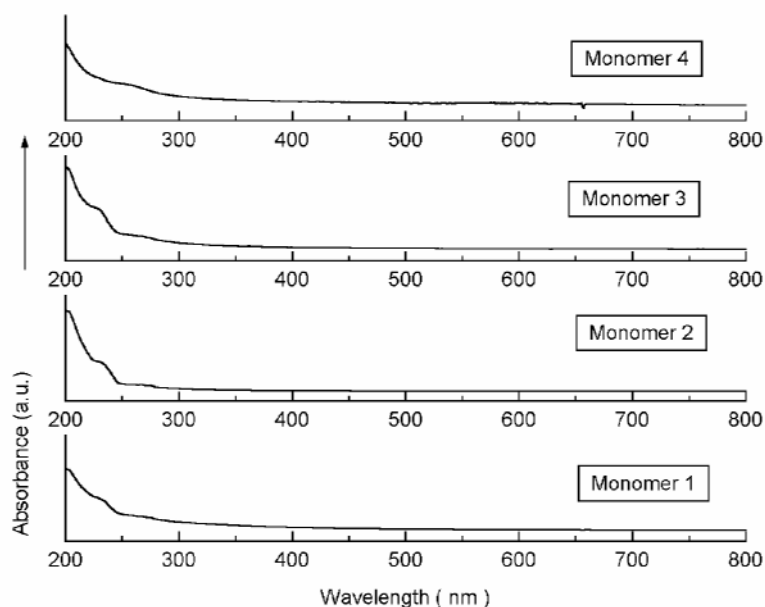

Fig. 6. UV-vis spectra of the new material

The UV-spectra of the new materials prepared by 4 monomers are identical. The maximum absorption peak of the new product is below the wavelength of 200 nm and this behavior is the same as from PPX described in the literature [9].

On the Table 2 are the results of the elemental Analysis from the new product prepared by 4 monomers.

Table 2. *Elemental content of the new product*

Content %	C	H	O
PPX (theoretical)	92.26	7.74	
Product 1	90.69 ± 0.08	8.01 ± 0.01	0.33 ± 0.00
Product 2	93.50 ± 0.25	6.69 ± 0.01	0.28 ± 0.01
Product 3	90.58 ± 0.40	6.79 ± 0.03	0.40 ± 0.01
Product 4	92.09 ± 0.10	6.98 ± 0.04	0.24 ± 0.18

The elemental content of the new product lies in the order of the theoretical calculation for PPX. It shows a small content of oxygen by all the new products. The reason for oxygen content is due to side product, which remains by the new product event after thermal treatment. All the results above could confirm that PPX could be prepared by the monomers based on ether-compounds.

Concerning the reaction mechanism during the CVD-process, it is to expect that the reaction could occur after equation in Fig. 7.
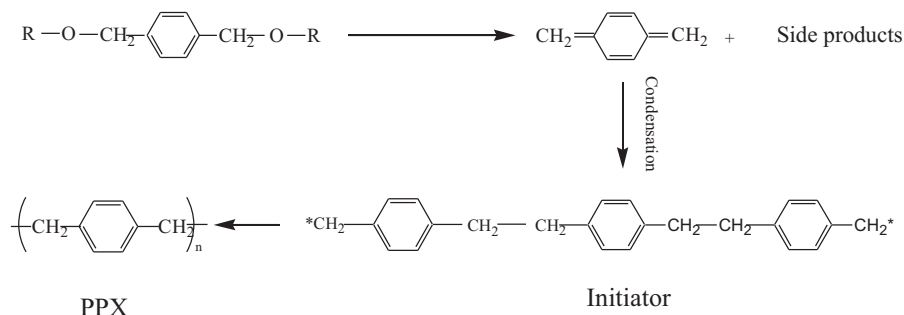

Fig. 7. Reaction mechanism by the CVD-process

It is well-known that the formation of PPX by pyrolysis of paracyclophane proceeds by cleavage of the ethylene bridge of paracyclophane and with the formation of quinodimethane. These species are highly reactive and undergo spontaneous polyreaction during the course of physical condensation on cool substrates [3, 6]. For these monomers as starting material, the C-O-C bonding were obviously attacked and broken by the pyrolysis so that the quinodimethane were formed during the CVD-process. Identifying the side products are always a difficult task because of the small amount. The side product, but surely depends on the starting monomer. Fig. 8 shows the IR-spectra of the side product prepared by monomer 1 and 2.

To get the side products, the sample was washed with methyl chlorine. It is clearly to see that for the two monomers as starting materials, the IR-spectra consist of the IR-spectrum of the unreacted monomer and of the side product. The strong absorption peak at 1103 cm^{-1} is assigned to the absorption of C-O-C group of the unreacted monomer. The side products of these monomers have the same strong absorption peak at 1701 and 1609 cm^{-1}, which could be assigned to the C=O and C=C group. In difference to the side product prepared by monomer 1, the two strong absorption peaks at 770 and 745 cm^{-1} were observed by the side product prepared by monomer 2. Although we do not identify the side products, they, however, could be removed by thermal treatment.

As mentioned above, the side products were formed by the CVD-process, so that the quality of the prepared PPX could strongly depends on both the properties of the monomer and the side product such as the boiling point and the CVD-condition such as the pyrolysis temperature, the substrate temperature. Fig. 9 shows the IR-spectra of the material prepared by monomer 1 by different pyrolysis temperature.

It is clearly to see that a strong absorption peak at 1103 cm^{-1}, which is assigned to the C-O-C absorption peak from unreacted monomer, was observed by the pyrolysis temperature of 650°C. This means that a big amount of unreacted monomer remain after CVD-process. With increasing pyrolysis temperature, this peak becomes weaker. This tendency is observed for all 4 monomers as starting
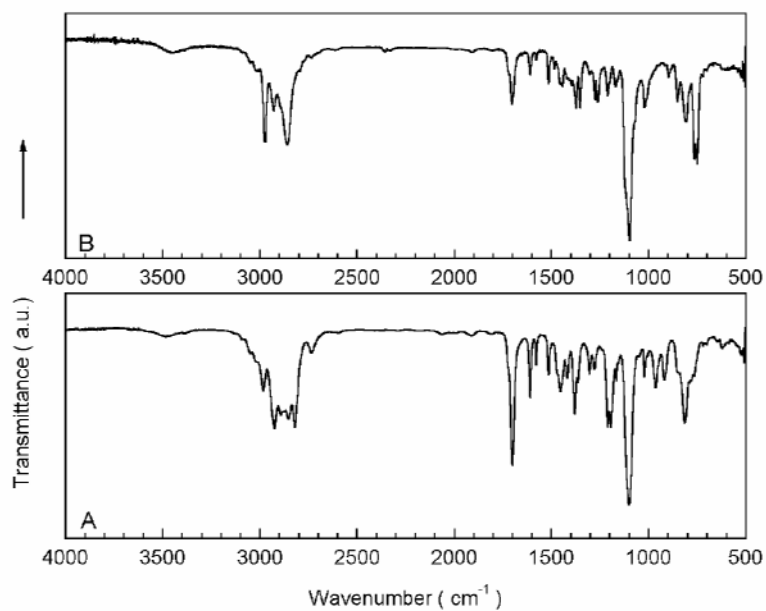
Fig. 8. IR-spectra of the side product, (A): prepared by monomer 1, (B): prepared by monomer 2
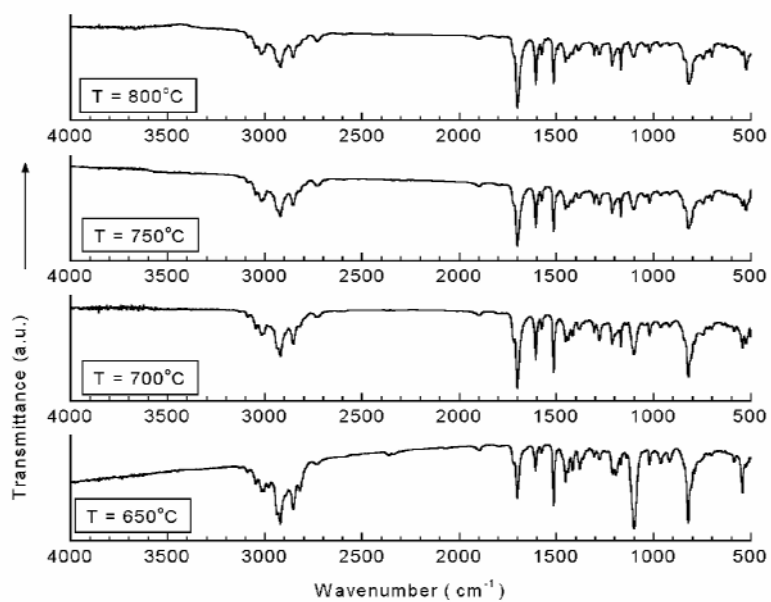

Fig. 9. IR-spectra of the material prepared by different pyrolysis temperature

materials. This result indicates that the reaction in Fig. 7 is favorable by high pyrolysis temperature. Concerning the influence of the substrate temperature, Fig. 10 shows the IR-spectrum of PPX prepared by monomer 3 and by cold substrate temperature.
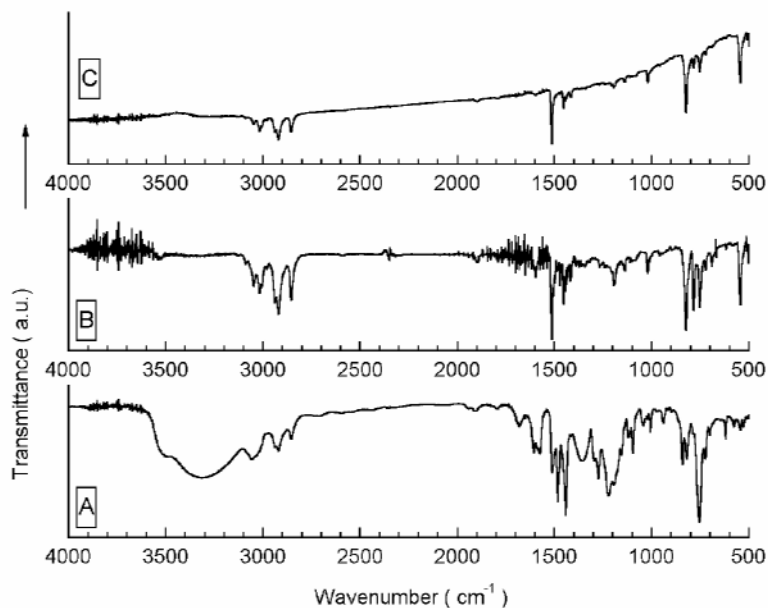

Fig. 10. IR-spectra of the material prepared by different position in deposition zone, (A): top position, (B): middle position, (C): end position

The substrate was placed on different position, at the top, middle and the end of the deposition zone. It is clearly to see that the sample at the top position was strongestly contaminated by the side product. A least contamination of the side product was observed at the end position. This result indicates that the unreacted monomer and side product mainly condense by cold substrate temperature at the top position. It occur a cold trap of the side product by cold substrate temperature. Unlike the monomer 1, 2 and 4, the side product from monomer 3 contains the strong broad absorption peak at 3400 cm^{-1}, which can be assigned to the absorption peak from hydroxyl group. The reason is due to the differences in the structure of the starting monomer. The monomer 3 is a aromatic ether and the other 3 monomer are aliphatic ether. In the case of monomer 3, it is difficult to remove the side products by thermal treatment. After thermal treatment, the sample seems to be brown and not transparent. In the elemental analysis, the product prepared by monomer 3 has the highest Oxygen content compared to the other products. In this case, the sample must be washes with methyl chlorine before drying to improve the quality of the material.

Concerning the structure and the thermal properties of PPX prepared by this monomers, the X-ray diffraction, TGA and DSC investigation were performed by PPX prepared by monomer 1.
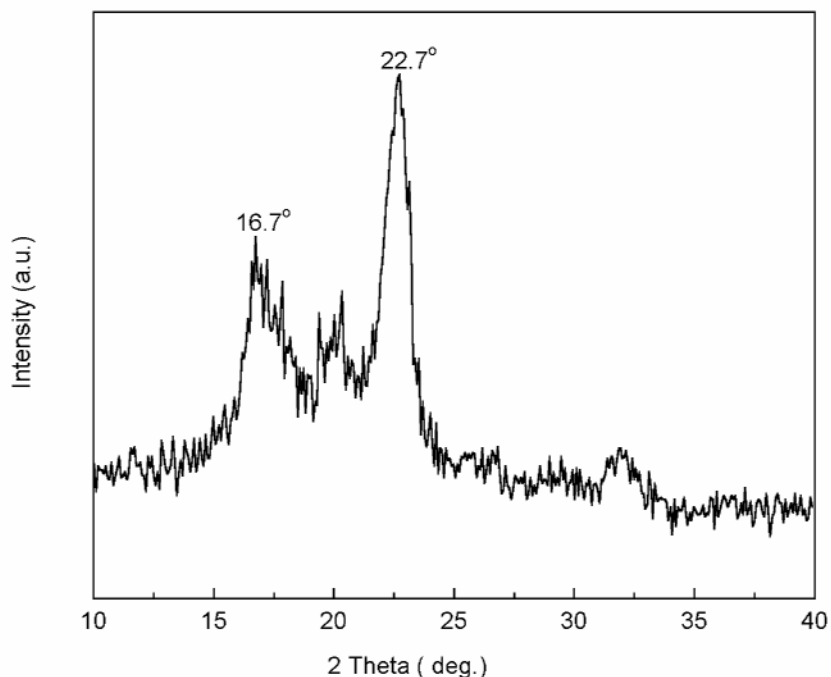
Fig. 11 shows X-ray diagram of PPX.

Fig. 11. Wide angle X-ray diagram of PPX

It is clearly to see the two strong peak at 16.7° and 22.7°. This result strongly implies that the prepared PPX is semicrystalline. For the calculation of the crystallinity of the polymer from X-ray diagram, it was used a first approximation by

$$X_c = A_c/(A_a + A_c)$$

Where X_c is the crystallinity, A_c the area under the crystalline peak and A_a the area under amorphous hump. For this case, X_c is equal about 62% compared to 60% reported by [1].

Fig. 12 shows the TGA-thermogram of PPX.

PPX is under N_2-atmosphere thermal stable till about 280°C. Above 280°C, it begins to lose their weight. On the temperature of 480°C, a strong weight loss of PPX was observed. The material decomposites on this temperature.

Finally, Fig. 13 shows the DSC-thermogram of PPX.

It is to note that the glas temperature of PPX is about 65°C. The melting process of PPX shows a characteristic behavior. It is to observe 3 transition peak

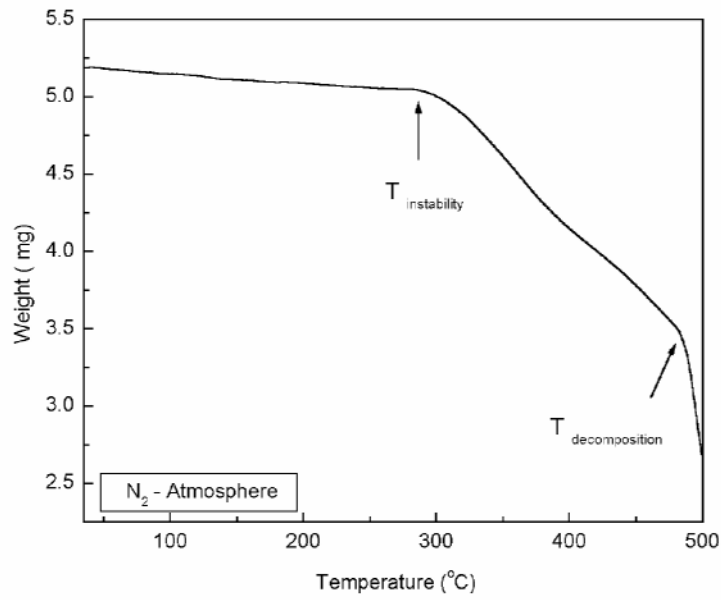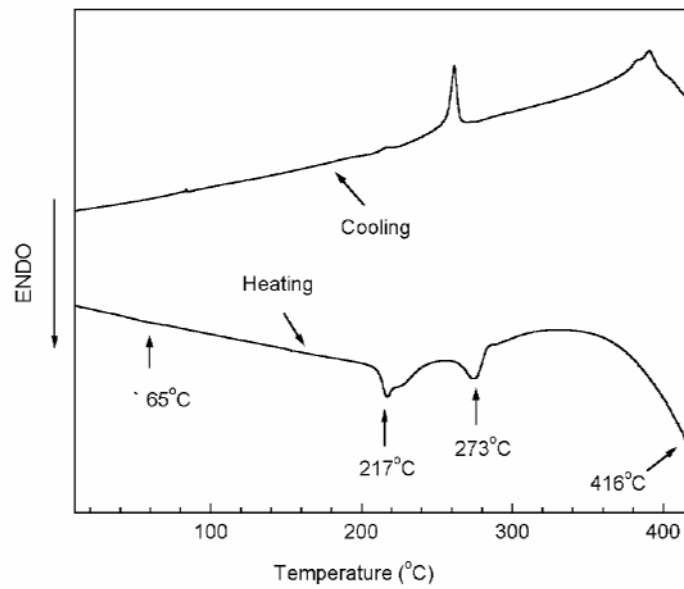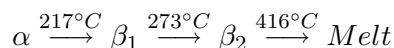**Fig. 12**. TGA-thermogram of PPX

Fig. 13. DSC – Thermogram of PPX

at 217, 273 and 416°C. In the literature [10-12] is well known that PPX has 3 form of crystallit α, β_1, β_2. The α-form has a monoclinic cell structure, β_1 and β_2 has a hexagonal cell structure. The melting process of PPX is to undergo two crystalline phase transition:

$$\alpha \xrightarrow{217°C} \beta_1 \xrightarrow{273°C} \beta_2 \xrightarrow{416°C} Melt$$

The DSC result could reconfirm two crystalline phase transition of PPX by the melting process. The $\alpha - \beta_1$ phase transition was reported normally to be irreversible by Niegish [13]. The recent work [14] indicates that a reversible $\alpha - \beta_1$ phase transition can be achieved by annealing for an extended period of time (12 h) at sufficiently high temperature (352°C). By the cooling curve was observed only two transition peak, which correspond to the melt $- \beta_2 - \beta_1$ transition. In this case, the $\alpha - \beta_1$ phase transition undergo irreversible. It is interesting to note that the melting point of β_2 phase lies in the region of thermal instability of PPX ($T > 280°C$). That means that the melting process of PPX is accompanied by decomposition.

4. CONCLUSION

PPX could be prepared by the monomer based on ether-compounds via CVD-method. This is one-step process. There are side products by the CVD process and it depends on both the starting materials and the CVD-condition. The side product could be removed by thermal treatment. For all the four monomers as starting material, the reaction will be favorable at high pyrolysis temperature of about 800°C. The results of the investigation of the PPX prepared by new monomers regarding the structure and thermal properties provide a good agreement to the PPX prepared by the other route.

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