

A Preliminary Study on the Synthesis of Poly(Vinylbenzyl Chloride) with Different Solvents

(Kajian Awal Sintesis Poli(Vinilbenzil Klorida) menggunakan Pelarut yang Berbeza)

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ABSTRACT

Polyvinyl benzyl chloride (PVBC) was synthesized by free radical polymerization of 4-vinylbenzyl chloride using benzoyl peroxide initiator at 60 °C. PVBC was synthesised in different solvents such as toluene, xylene, 1,4-dioxane, and tetrahydrofuran. The polymers were structurally characterized by ¹H NMR and FTIR spectroscopic techniques. The thermal property of the polymer was investigated by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA). The number average molecular weight, weight average molecular weight and polydispersity index of PVBC synthesised in different solvents were determined and compared by gel permeation chromatography technique.

Keywords: Polymer synthesis; polyvinyl benzyl chloride

ABSTRAK

Poli vinilbenzil klorida (PVBC) disintesis melalui pempolimeran radikal bebas daripada 4-vinilbenzil klorida dengan menggunakan pemula benzoil peroksida pada 60 °C. PVBC disintesis dalam pelarut yang berbeza seperti toluena, xilena, 1,4-dioksana dan tetrahidro furan. Pencirian struktur polimer dibuat menggunakan teknik spektroskopi ¹H NMR dan FTIR. Sifat terma polimer dikaji menggunakan analisis termogravimetrik (TGA) dan analisis termogravimetrik pembezaan (DTA). Berat molekul purata nombor (Mn), berat molekul purata berat (Mw) dan indeks polisebaran PVBC disintesis dalam pelarut berbeza telah ditentukan dan dibandingkan dengan teknik kromatografi penelapan gel (GPC).

Kata kunci: Poli vinilbenzil klorida; sintesis polimer

INTRODUCTION

Polymers are important materials with many distinct applications. Polymer materials can be developed with many attractive properties, such as controlled chain length, multifunctionality and tunable chemical properties. Developments of new polymerization methods in the early 1990s followed by the efficient organic synthesis methods adopted to polymer science in the early 2000s have made a remarkable effect on the progress of polymer synthesis and polymer functionalization (Daglar et al. 2020). The styrene monomer was discovered by Newman. Polystyrene first polymerised by Eduard Simon in 1839 and started synthesizing commercially in 1925 (Scheirs et al. 2003). Vinyl benzyl chloride (VBC) is chloromethylated polystyrene and is one of the most important bifunctional monomers. The presence of chlorine at fourth position

and vinyl group at first position makes VBC polar and polymerizable, respectively. The benzylic chlorine and benzene ring present in the hydrocarbon polymer chain, makes a large number of nucleophilic and electrophilic substitution reactions possible for PVBC. Moreover, synthesise of functionalized polymers becomes relatively easy with this.

Direct free radical polymerization of VBC is the common reaction to synthesis PVBC. On top of that, PVBC can be homopolymerized or copolymerized with different co-monomers by the radical polymerization method (Kondo et al. 1979). Moreover, PVBC polymer is one of the commonly used polymers for ion exchange membranes (Jeevanantham et al. 2018), water electrolyzers (Coppola et al. 2020; Vengatesan et al. 2015), redox flow batteries (Park et al. 2012), and fuel cell membranes (Luo et al. 2010; Yu et al. 2018).

Previously, PVBC was formed by the chloromethylation of polystyrene. Chloromethyl methyl ether, bis(chloromethyl) methyl ether, chloromethyl ethyl ether and their bromo analogues are the most efficient chloromethylating agents. However, the chloromethylation reaction is usually not preferred due to the highly toxic nature of these reagents and the lack of precise control over the degree and location of functionalization (Moulay et al. 2018; Zhang et al. 2010). A safer alternative method to prepare chloromethylated polymers is the polymerization of chloromethylated vinyl monomers. On account of the fact that, vinyl monomer contains chloromethyl groups in its structure, the chloromethylation step can be avoided. Thus, PVBC synthesised directly from VBC avoids the harmful chloromethylation process (Vengatesan et al. 2015).

Different research groups have carried out synthesis of homopolymer and copolymers of VBC in different solvents. We have synthesized PVBC in our laboratory by the free radical polymerization of VBC using benzoyl peroxide initiator, in xylene solvent at 80 °C (Mathew et al. 2018). Another research group developed anion exchange resins of (vinyl benzyl chloride-divinyl benzene) copolymers for water treatment. The copolymer synthesised in tetrahydronaphthalene, xylene and a 1:1 mixture of tetrahydronaphthalene and xylene solvents to determine the influence of these solvents on resulting polymer (Ezzeldin et al. 2010). Microporous poly (styrene-co-divinylbenzene) synthesised by precipitation copolymerization of VBC and divinylbenzene (DVB) with azobis(isobutyronitrile) in acetonitrile solvent at 60 °C (Cormack et al. 2012). The reversible addition-fragmentation chain transfer (RAFT) polymerization of methylmethacrylate and VBC were carried out in toluene solution at 75 °C for 48 h using benzoyl peroxide (BPO) as the initiator (Faghihi et al. 2017). However, a comparison of the role of different solvents in the synthesis of PVBC is not studied yet.

In the present work, the synthesis of PVBC from VBC in different solvents has been studied. Moreover, toluene, xylene, tetrahydrofuran (THF) and 1, 4-dioxane were employed as the solvents. These solvents differ in their structure and polarity. This study includes solvents such as THF and 1, 4-dioxane which are more polar and less toxic than toluene and xylene. Furthermore, the study aims to determine the effect of these solvents on mass recovery of PVBC synthesised at low temperature (60 °C). Besides, molecular weight and polydispersity of the polymer synthesised in each of the solvents are investigated.

MATERIALS AND METHODS

MATERIALS

4-vinylbenzyl chloride (90%) was purchased from Sigma Aldrich and used as the monomer. It was purified by passing through a short column of basic alumina. Benzoyl peroxide (15% water) purchased from Sigma Aldrich was used as initiator. Commercially available xylene, tetrahydrofuran, toluene, 1, 4-dioxane and methanol were used as received.

POLYMER SYNTHESIS

One gm of VBC monomer and 15 mL of THF solvent were taken into a three neck round bottom flask fitted with a reflux condenser. The mixture was allowed stirring for 15 min and BPO was added as radical initiator (3%). The polymerization was conducted under a nitrogen atmosphere at 60 °C for 43 h with stirring. After the polymerization completed, the polymer was precipitated by pouring to cold methanol solution. The resultant polymer was dissolved in chloroform and precipitated in methanol again, washed several times with methanol and then dried in a vacuum oven at 60 °C for 24 h. The same procedure of polymerization, precipitation, and purification are repeated with same mass of VBC and BPO and same volume of 1,4-dioxane, xylene and toluene solvents under similar temperature and time.

INSTRUMENTATION

Gel Permeation Chromatography (GPC, Waters 2414 refractive index detector, styragel mixed bed columns) using THF carrier with a flow rate of 1 mL min⁻¹ was used to determine the molecular weight and molecular weight distribution of PVBC synthesised in different solvents. The infrared spectrum (IR) was recorded using a Perkin Elmer Spectrum GX spectrophotometer (Perkin Elmer, Waltham, MA, USA) in the range of 500-4000 cm⁻¹.

Nuclear Magnetic Resonance experiments were performed on a Bruker 400 MHz instrument using CDCl₃ as the solvent at room temperature in the range between δ = 0-10 ppm.

Thermogravimetric analysis was carried out using a mettler Toledo TGA851/LF/1100 thermogravimetric analyser by heating the samples from room temperature to 650 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

RESULTS AND DISCUSSION

The polymerization of VBC monomer to PVBC polymer, carried out by free radical polymerization. The polymerization of VBC was performed at 60 °C in different organic solvents such as THF, xylene, toluene and 1, 4-dioxane, using BPO as the radical initiator. The conditions of synthesis in different solvents and the mass recovery of PVBC obtained are given in Table 1. The PVBC polymerization experiments with each type of solvent were repeated many times. The standard deviation for the polymerization with solvents, THF, xylene, toluene and 1, 4-dioxane are 0.0029, 0.0038, 0.0047, and 0.0041, respectively. The polymerization in each solvent was carried out with 3% of BPO initiator for 48 h to obtain better mass recovery. The highest mass recovery obtained is with THF followed by xylene and then 1, 4-dioxane. This may be due to the more polar nature of THF and 1, 4-dioxane when compared to toluene and xylene (Valdebenito et al. 2010). Furthermore, VBC and PVBC are also polar compounds due to the chloromethyl groups present in them. Hence, the more polar THF and 1, 4-dioxane can interact more efficiently with polar chloromethyl groups in the growing polymer chain than the less polar toluene and xylene (Ezzeldin et al. 2010). Accordingly, THF, 1, 4-dioxane and xylene solvents made low temperature (60 °C) synthesis of PVBC possible, with good mass recovery. In addition, xylene gives comparatively good mass recovery at high temperature (80 and 90 °C) and at low temperature. Moreover, this research focuses primarily on the comparison of effect of the solvents on polymerization of VBC at low temperature (60 °C). The conversion of VBC to PVBC is represented in Scheme 1.

The molecular weights and polydispersity of the, PVBC synthesised was determined by gel permeation chromatography (GPC) as shown in Figure 1. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) of PVBC synthesised in different solvents are listed in Table 2.

PDI can be obtained from (1). Interestingly, lower PDI of 2.1 obtained with THF solvent and higher PDI of 3.8 with 1,4-dioxane solvent. Moreover, the PDI values for xylene and toluene were 2.4 and 3.1, respectively. The retention time for the polymer synthesised from different solvent were found to be almost the same in the GPC curves.

$$PDI = \frac{M_w}{M_n} \quad (1)$$

The polymerization of VBC to PVBC was confirmed by ^1H NMR spectroscopy. The solvent used was CDCl_3 and TMS taken as the internal reference. The peaks from $\delta = 6.3\text{--}7.0$ ppm belong to aromatic carbons. The peak at $\delta = 4.5$ ppm is the chloromethyl peak. The low field lines occur at $\delta = 1.4\text{--}2.3$ ppm is due to alkane hydrogens of the polymer main chain. The peak at $\delta = 7.2$ is due to CDCl_3 (Hao et al. 2018). ^1H NMR spectra of PVBC synthesised in THF solvent is shown in Figure 2.

The FTIR spectrum was analysed to identify the structure of the PVBC. The FTIR spectrum obtained is shown in Figure 3. The FTIR spectrum of PVBC, synthesised in THF which gave optimum mass recovery (99.7%) and polydispersity of 2.1. The peaks appear at 676 and 1266 cm^{-1} are due to C-Cl stretching and $-\text{CH}_2\text{Cl}$ wagging vibrations of the $-\text{CH}_2\text{Cl}$ groups present in PVBC. The main chain of $-\text{CH}_2$ is responsible for the sharp peak at 2900 cm^{-1} in FTIR spectrum. The absorption band at 1511 cm^{-1} and other bands between 1400-1600 cm^{-1} belong to vibrations of aromatic ring present in PVBC (Mathew et al. 2018; Vengatesan et al. 2015).

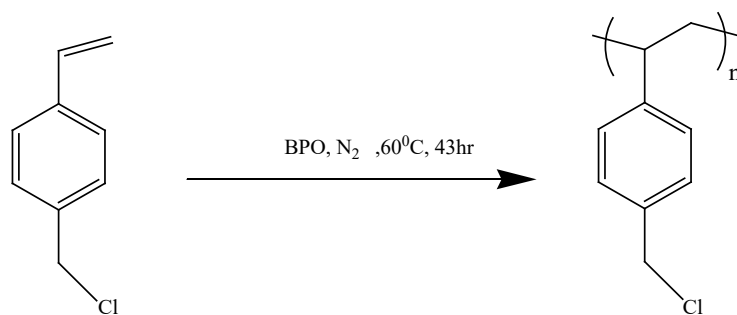
TGA studies of PVBC was carried out and TGA and DTA curves for PVBC are shown in Figure 4. There are two regions of weight loss. The first step occurs between 350 °C and 420 °C with a weight loss of 37.6%, is due to polymer main chain degradation. The second step occurs between 450 °C and 650 °C is due to the carbonization (Coppola et al. 2020; Lu et al. 2015). The TGA curve shows that the polymer has thermal stability up to 275 °C and can be used for applications until this temperature.

TABLE 1. Conditions of synthesis and mass recovery obtained for PVBC

Solvent	Reaction time (h)	Temperature (°C)	Mass recovery (%)
Tetrahydrofuran	48	60	99.7
1,4-dioxane	48	60	61.23
Xylene	48	60	60.38
Toluene	48	60	42.07

TABLE 2. M_n , M_w and polydispersity index of PVBC

Solvent	M_n	M_w	PDI
Tetrahydrofuran	3300	6900	2.1
1,4-dioxane	7000	26700	3.8
Xylene	10500	24700	2.4
Toluene	6400	19600	3.1



SCHEME 1. Synthesis of PVBC

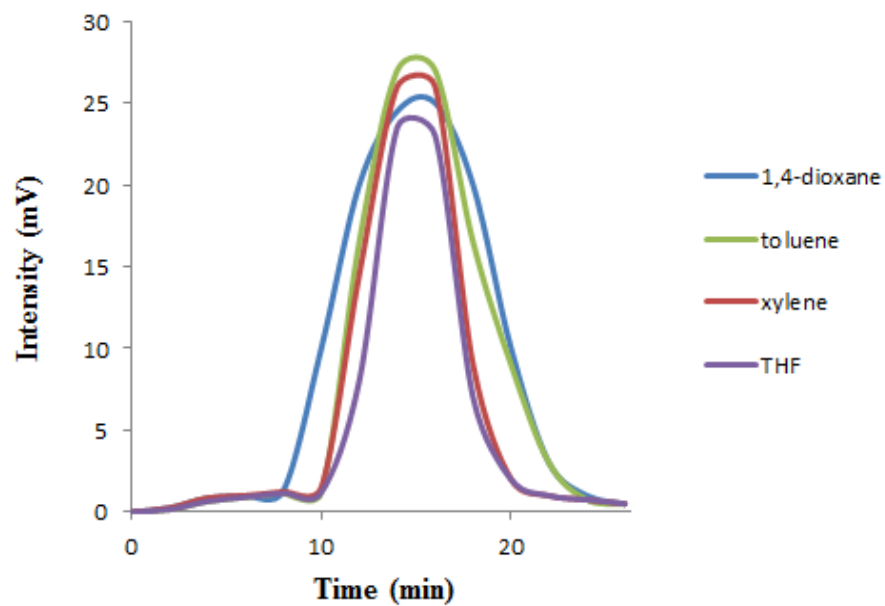


FIGURE 1. GPC chromatogram of PVBC synthesised in THF, Xylene, Toluene and 1, 4-dioxane

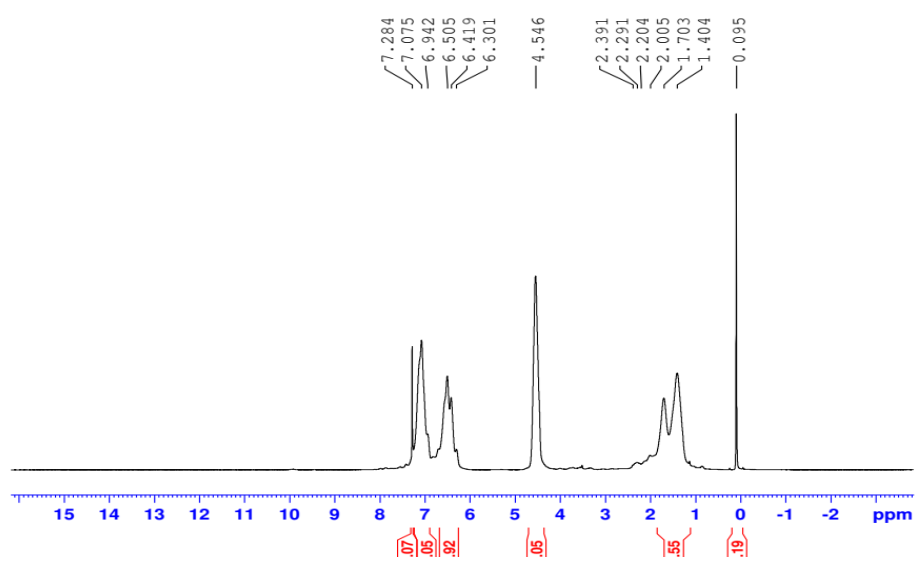
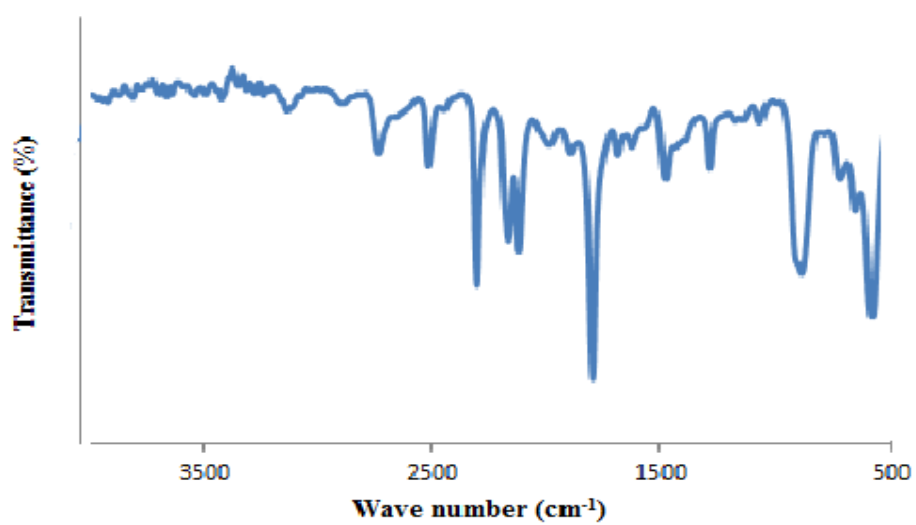
FIGURE 2. ¹H NMR spectrum of PVBC (prepared in THF solvent)

FIGURE 3. FTIR spectrum of PVBC

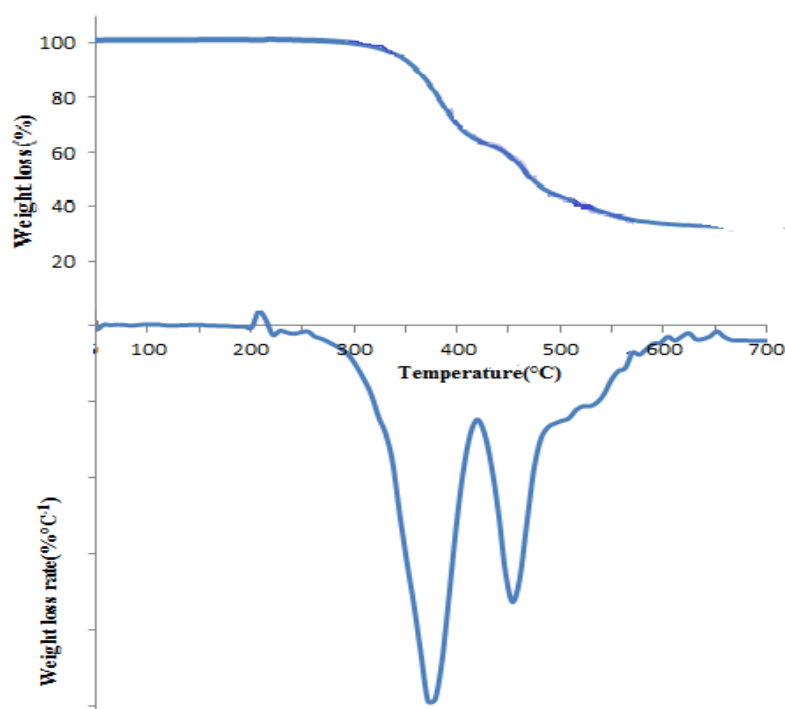


FIGURE 4. TGA and DTA curves for PVBC

CONCLUSION

Poly(vinylbenzyl chloride) was successfully synthesised using different solvents by free radical polymerisation. The molecular weight of the polymer synthesised in different solvents analysed by GPC. Higher mass recovery was obtained with THF solvent. The conversion of PVBC structurally confirmed by ^1H NMR and FTIR spectroscopy. The thermal properties of the polymer were determined with TGA and DTA curves obtained from thermal analysis. The TGA thermograms showed that the polymer has thermal stability up to 275 °C.

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