

Synthesis of Poly(vinylbenzyl chloride) (PVBC) and Temperature Effect

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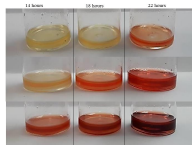
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GRAPHICAL ABSTRACT



Color changes from 14 hours, 18 hours and 22 hours at different temperature

ABSTRACT

One of the versatile radical polymerization techniques, the reversible addition fragmentation chain transfer (RAFT) process, was used to synthesize the bifunctional monomer, vinylbenzyl chloride (VBC) into poly(vinylbenzyl chloride) (PVBC). The RAFT polymerization technique is widely used because of the commercially available RAFT agents in the country. The right choice of the RAFT agent will result in a good polymerization. Temperature of 60°C, 70°C and 80°C were chosen in this research study. The other conditions such as the purging and reaction time, the ratio of monomer/initiator for the control of VBC polymerization were kept constant for all reactions. The reactions were monitored by ¹H nuclear magnetic resonance spectroscopy (NMR) in the presence of chloroform as the internal standard and also Fourier Transform infrared (FTIR). The characterizations using those two instruments were further discussed in the discussion part. The highest monomer conversion was 69% at 80°C for 22 hours.

Keywords: vinylbenzyl chloride, RAFT polymerization, temperature effect

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1. INTRODUCTION

Many polymers are employed for various uses for environment, life and the future. For instance, polymers are popular with the injection-molded plastic. One of the monomers, vinylbenzyl chloride (VBC) is one of the unexceptional monomers that can easily be functionalized with the presence of the pendant chlorine atom in the molecule. The functionalized polymers are not limited to the fire retardants, selective sorption resins, chromatography area and phase transfer catalysts [1]. The poly(vinylbenzyl chloride) (PVBC) has been used for wide applications such as amphiphilic block copolymers, hydroxide conducting polymers, membranes of the fuel cells, chromophores-bearing copolymers, antibacterial agents, and stimuli responsive composite nanoparticles [2].

The VBC can undergo polymerisation with controlled radical polymerisation, and it is called as the living radical polymerisation. The techniques for this polymerisation are reverse addition-fragmentation chain transfer (RAFT), atom transfer radical polymerisation (ATRP), nitrogen mediated polymerisation (NMP) [3]. Since the reactive C=X double bonds towards the addition of radicals represented is based on the addition fragmentation transfer agents, thus the RAFT technique becomes this research focus. Polymerization of well-defined poly(vinylbenzyl chloride) (PVBC) can be obtained when applying the living radical polymerizations. The majority of RAFT initiators can be widely categorized as xanthates, trithiocarbonates, dithiocarbamates, dithioesters, and dithiophosphonates that has been evolved and synthesized.

Due to this wide categorization of the RAFT agents, it needs to be carefully tailored to match the best conditions by varying the aromatic, alkyl group, and/or the good leaving group in the monomer. The role of the R and Z groups of the RAFT agents are well understood in relation to their effect on polymerization of monomers, their reaction kinetics, and polymerization conditions required. 4,4'-Azobis(4-cyanovaleric acid) or ACPA, can be used as an initiator, as it is a slightly yellowish white compound, water soluble [4] at pH more than 7, might be one of the useful compounds in research as a compound that has azo group, which decomposes in the presence of heat and/or light, [5] and the formed carbon radicals are reactivity excellent and helpful in polymerization and halogenation reactions of different vinyl polymer types.

This study will emphasize the temperature effect of VBC during polymerization process via the RAFT polymerization technique. The effect of different temperatures on the efficiency of polymerization can give rise to various effect towards the polymer properties itself. It is crucial to understand the kinetics and mechanism of the polymerization to get a desired polymer with specific properties such as glass transition, brittleness and toughness. In some polymers, the increment and decrement can ultimately lead the progressive degradation. Each monomer has its own effective temperature for the polymerization to occur. There are recent works about the RAFT homopolymerisation of PVBC on the kinetic aspect and modification of the copolymer using VBC where the

polymerization of VBC was conducted under constant temperature with various reaction times and different monomer:initiator:RAFT agent ratio. However, the work on the PVBC homopolymer with three mostly used temperatures for polymerization has not been reported.

2. EXPERIMENTAL

In the round bottomed flask, CPADB (0.0032, mol) and ACPA (0.0390 mg, mol) were dissolved in vinyl benzyl chloride (2mL, mol) and purged with N₂ for 30 minutes. The oil bath was preheated during 40 minutes of purging. The reaction mixture was immersed and heated at 60°C, 70°C and 80°C for 22 hours, 18 hours and 14 hours for each respective temperature. After the hours of reaction, the round bottomed flask was exposed to air to stop the polymerization and the polymer was precipitated out using cold methanol. Later, the polymers were analysed using ¹H NMR and FTIR spectroscopy.

3. RESULTS AND DISCUSSION

3.1 Synthesis of poly(vinylbenzyl chloride) (PVBC)

The vinylbenzyl chloride (VBC) was chosen as the focus of study due to its dual functionality at the end of the monomer. The living character responsibility; RAFT agent that present at the polymeric end chain of polymer is the highlight of the RAFT polymerization [6]. Lowe and McCormick (2007) stated that the controlled polymerization of monomer came from a good choice of RAFT agent. In this experiment, the purging purpose was to eliminate the presence of oxygen in the system that will cause initiation and inhibition and the results would be intriguing [7]. The time taken was to make sure that all oxygen was eliminated out completely from the system referring to the capability of oxygen to quench the initiator excited states. [8].

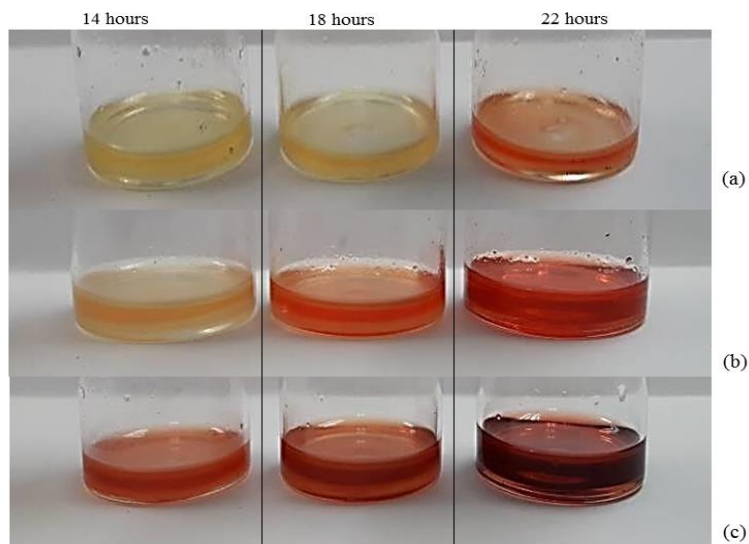


Figure 1 Color changes from 14 hours, 18 hours and 22 hours for the temperature of (a)60°C, (b)70°C and (c) 80°C respectively.

Figure 1 shows the colour changes at different temperature. From the above observation of colour changes of the crude product, there were changes in colour from the lower temperature to the high temperature of product. For information, the mixture at t=0 (before conducting the experiment) was pink coloured due to the RAFT agent and CPADB. The colour changes from t=0 to each the time of reaction took place individually for each respective

reaction. Visual comparison confirmation of the colour of the polymers before and after end group removal is very useful. The end group has successfully been removed as the RAFT groups are observed in coloured and vice versa [9]. The colour of pure product is always retained after the washing with cold methanol often represent the present of RAFT agent. Based on the observation, the colour for each experiment was different. For the 14 hours of 60°C reaction, the colour from $t=0$ to $t=14$ were in yellow. This is due to the degradation of RAFT agent. The crude mixture with the highest temperature and the longest time (80°C, 22 hours) appeared to be darker in colour compared to the other eight reactions. Normally, the colour will decrease once it achieves to the higher temperature due to instability.

3.2 Polymer Characterizations

3.2.1 NMR Characterizations

^1H NMR was used to determine the formation of the polymer backbone ranging from 0.6 ppm up to 2.3 ppm for the polymerisations of VBC. Figure 2 is the representative for the crude PVBC, where the peak of the polymer backbone at 1.3 ppm until 2.3 ppm are apparent. For the crude PVBC, the signal referring to the vinylic protons of VBC monomer ((a) and (b)) were observed at 5.3–5.8 ppm. The benzene signal of residual monomer and the crude polymer was overlap due to broad polymer signal (c) and could be seen at 7 ppm to 7.5 ppm. A signal at 4.5 ppm corresponded to the both of CH_2 monomer and polymer peak overlapped together. The signal at 0.8–2.5 ppm was attributed to the CH protons ((1 + 2) of the polymer backbone.

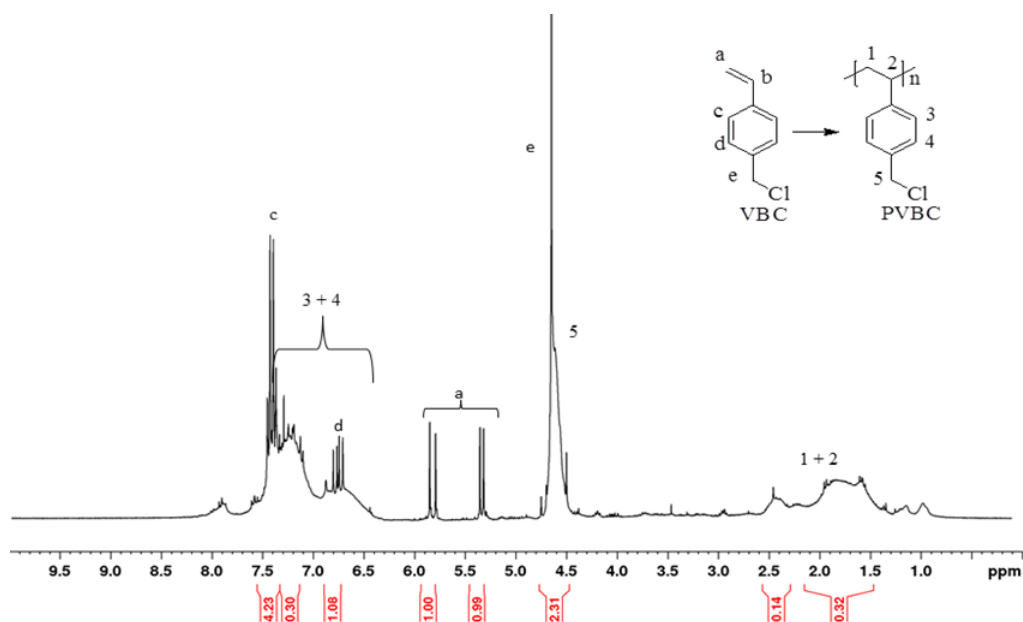


Figure 2 ^1H -NMR spectrum of crude PVBC.

Polymer NMR integration is important, and it can determine the monomer conversion. The calculation of the VBC monomer conversion can be calculated referring to the monomer peak and polymer peak. The peak at 4.5 ppm until 4.8 ppm ($\text{CH}_2\text{-Cl}$) is the overlapping of the monomer integration and the polymer integration ((e) and (5)). Thus, the area cannot be taken to determine the monomer conversion. Alternatively, the monomer conversion was determined using the integration from 2.3 ppm until 2.6 ppm. The equation of the monomer conversion calculated in percentage and the monomer conversion calculation data in percentage are shown as below.

Equation of % of monomer conversion

$$= \frac{\text{Integration from the polymer peak, } H_p}{\text{Integration from the monomer peak, } H_m + \text{Integration from the polymer peak, } H_p} \times 100\%$$

Table 1 Monomer conversion calculation data in percentage

Time (hours)	% of monomer conversion at	
	70°C	80°C
14	28	28
18	27	35
22	36	69

From the conversion in Table 1, it can be related to the colour of the crude mixture as aforementioned. At the temperature of 80°C at 22 hours of reaction, a crude mixture was produced with the highest percentage of monomer conversion.

3.2.2 IR characterization

The IR characterizations helped in determining the functional group of sp^3 -CH of the crude where the double bond of C=C of VBC forming a single bond C-C and sp^2 =CH from the pure VBC monomer itself. Figure 3 shows the IR spectrum for the VBC monomer. For the pure monomer, the CH sp^2 stretching, ranging from 3000 cm^{-1} to 3100 cm^{-1} and from spectrum, the monomer showed a peak at 3008 cm^{-1} . C=C vinylic appeared at 1669 cm^{-1} . Around those wavenumbers, there were several peaks indicating the CH aromatic compound. C=C aromatic bond peak was present at 1629 cm^{-1} and 1510 cm^{-1} . The stretch C-Cl bond can be found in the finger print region, 728 cm^{-1} . The data was tabulated in Table 2 that showed the characteristic of IR adsorption frequencies (wavenumber) of pure VBC monomer.

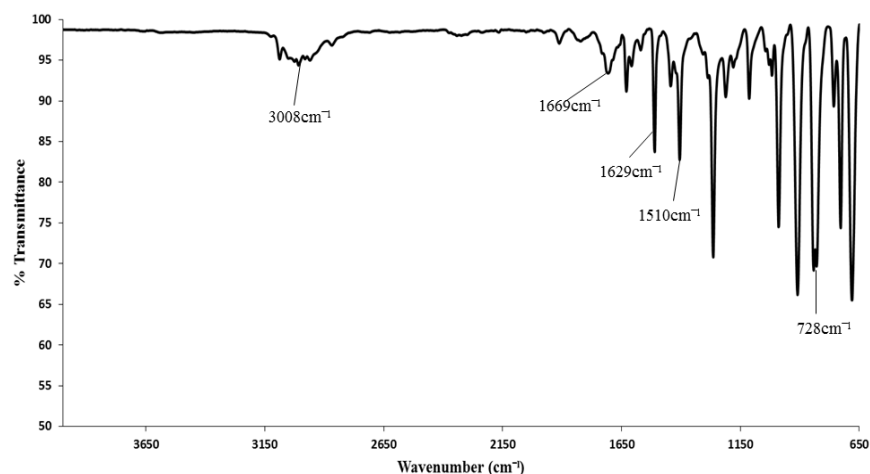


Figure 3 VBC monomer IR spectrum.

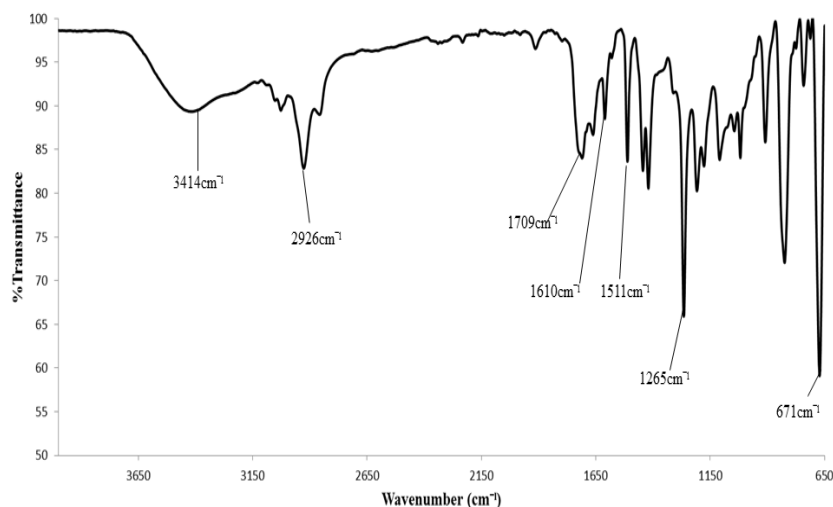


Figure 4 Crude PVBC IR spectrum.

Table 2 Characteristic of IR adsorption frequencies (wavenumber) of pure VBC monomer

Wavenumber (cm ⁻¹)	Intensity	Type of Vibration	Functional Group
3008	Medium	Stretch	sp ² =CH
1669	Medium	Stretch	C=C
1629, 1510	Medium	Stretch	aromatic C=C
728	Medium	Stretch	-C-Cl

After polymerization, there were some new bond appeared in the IR spectrum shown in Figure 4. The O-H bonded peak, C=O carbonyl peak and C-O bond from carboxylic acid probably come from the initiator and the RAFT agent itself during the polymerization. Table 3 showed the characteristic IR adsorption frequencies (wavenumber) of crude VBC polymer.

Table 3 Characteristic of IR adsorption frequencies (wavenumber) of crude VBC polymer

Wavenumber (cm ⁻¹)	Intensity	Type of vibration	Functional group
3414	Medium, broad peak	Stretch	O-H bonded
2926	Strong	Stretch	sp ³ -CH
1709	Strong	Stretch	C=O carbonyl
1610, 1511	Medium	Stretch	aromatic C=C
1265	Strong	Stretch	C-O carboxylic acid
671	Strong	Stretch	C-Cl

3.3 Temperature effect on poly(vinylbenzyl chloride) (PVBC)

Figure 5 shows the schematic reaction of PVBC at 60°C with the aid of ACPA and CPADB for three respective hours. The comparisons between the hours for each respective temperature are shown as below.

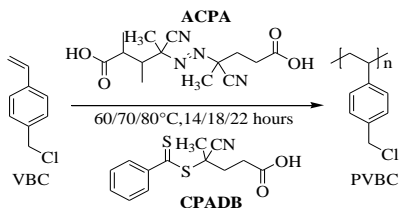


Figure 5 Schematic reaction of PVBC at 60°C, 70°C and 80°C.

From Figure 6 (a) and (b), there are no significance changes from 14 hours to 22 hours. The pattern of the above spectra showed that as the temperature increase, the polymerization rate becomes higher, thus the polymeric backbone forms much greater than the lower temperature.

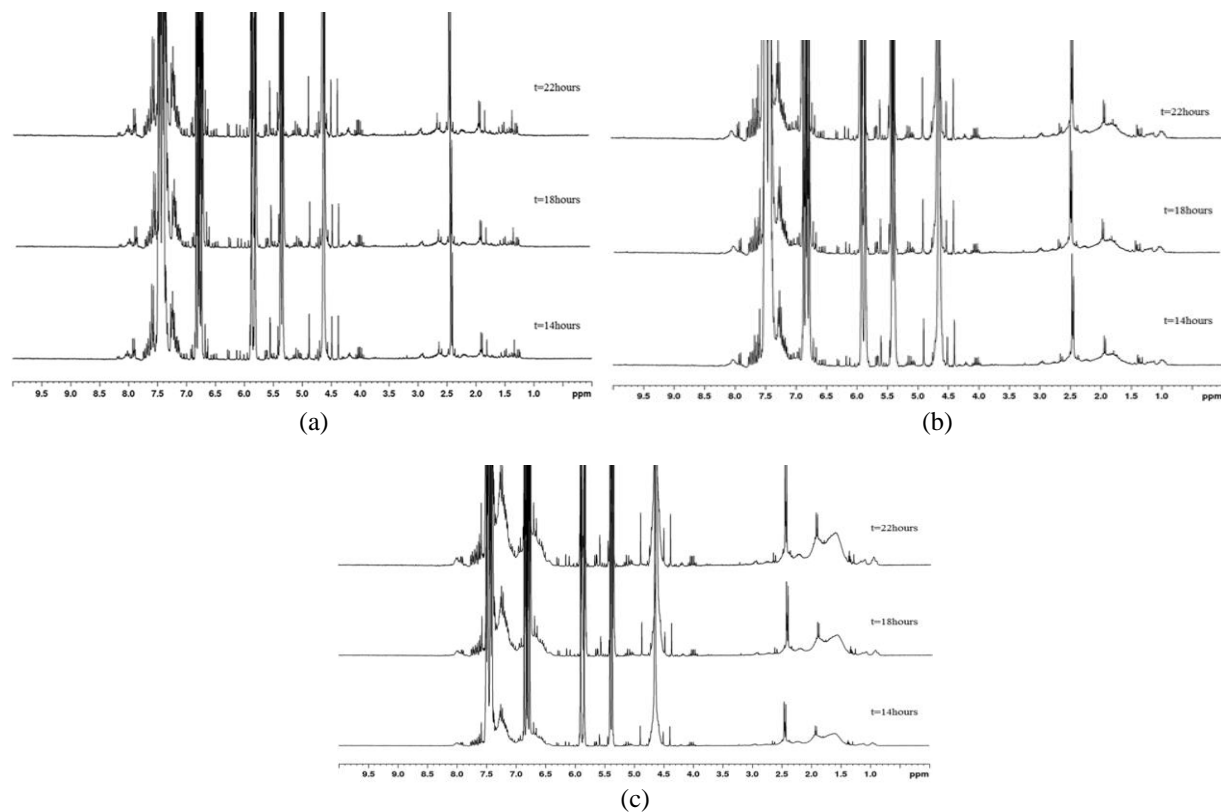


Figure 6 NMR spectra of crude PVBC at (a) 60°C, (b) 70°C, (c) 80°C, for 14 hours, 18 hours and 22 hours.

The initiator can form radical when the heat is applied due to the loss of stability and high energy. The reaction proceeded with the reaction between VBC monomer to form initiator –monomer radical. After sometimes, it reacted with the monomer in the system to form long chain polymeric radical with the ACPA attached to the

polymer. For the first polymeric radical chain, it underwent reversible transfer chain process where the first polymeric chain reacted with the RAFT agent, CPADB. The R group bond cleaved from the CPADB formed radical and a dormant chain consisting of polymer and Z group. This R group radical reinitiate with VBC monomer which is the second type of polymeric chain which the R group was attached to it. Both polymer that has different initiation ways, proceeded with the chain equilibrium step where both reacted with the dormant chain reversibly.

As seen in Figure 6 (a), the formation of the polymer backbone peak in the NMR spectrum was obscure probably because of initiation of the initiator that was insufficient to start the polymerization at 60°C and may also due to the retardation caused by cross-termination of very short radicals formed in the early stage of the polymerization. Instead of forming polymer, the formation of oligomers; short chain polymer, was formed. The monomer peak was apparently appeared on the spectra rather than the broad peak indicating the formation of polymer. Unlike the NMR spectra for the temperature of 80°C, the broad peak at the position of 1.3ppm up to 2.5ppm indicated the formation of C-C polymeric chain bond from the vinylic C=C of the VBC monomer once it was initiated. The probability first initiation and the re-initiation from the R group of the RAFT agent was high such that the reversible chain transfer step and the chain equilibrium step were favourable at 80°C.

4. CONCLUSION

In this study, the RAFT polymerization technique does show versatility of the technique using the RAFT agent and suitable initiator to generate highly conversion of monomer, which is useful for highly functional monomers and is suitable for VBC due to the presence of bifunctional groups. During the study, the synthesis poly(vinylbenzyl chloride) (PVBC) via RAFT polymerisation was successfully conducted with the aid of a RAFT agent and initiator and using a suitable ratio. Determination of the temperature effect towards polymerization and its conversion were also concluded as it can be determined using the integration from NMR spectra. The highest conversion had 69% at 80°C for 22 hours. The entire polymer obtained was able to be characterized using NMR and FTIR.

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