

SYNTHESIS AND CHARACTERIZATION OF POLY (N-VINYL PYRROLIDON – co-VINYL ACETATE)

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ABSTRACT

Copolymers of N-vinyl pyrrolidone (VP) and vinyl acetate (VA) were prepared by free radical polymerization in a solution of ethanol, using 2,2-azobisisobutyronitrile as an initiator. Properties of copolymers were characterized by spectroscopic IR method, and also DSC and Gel permeation chromatography (GPC) analyses. Effects of temperature, monomer concentration and initiator concentration on monomer conversion into copolymer were studied. The monomer conversion into copolymer is highest at the following conditions: reaction temperature: 70 °C, monomer concentration: 40 %, initiator concentration: 1,5 % (w/w) and reaction time: 250 min.

Keywords: copolymer, N-vinyl pyrrolidone, vinyl acetate, copolymerization.

1. INTRODUCTION

Copolymers of N-vinyl pyrrolidone (VP) and vinyl acetate (VA) monomers have significant utility in the cosmetic, pharmaceutical industries food industry and other technical fields [1]. In recent years, there has been an increasing interest in the synthesis and properties of VP/VA copolymers. Zhong et al. have been studied effect of the content of hydrophilic units in VP and hydrophobic units in VA on copolymers [2]. Mathakiya et al. studied synthesis VP/VA copolymer by free radical polymerization in a solution of benzene, using 2,2-azobisisobutyronitrile (AIBN) as an initiator [3]. Properties of copolymers were characterized by spectroscopic (IR, NMR) methods, and also TGA and element analyses. High homogeneous copolymers of VP and VA were prepared by Mohamad et al [4 - 5].

In this paper, VP/VA copolymers were prepared through free radical copolymerization in a solution of ethanol, using AIBN as an initiator. Characteristics of copolymers were studied by spectroscopic IR method, DSC and GPC analyses.

2. EXPERIMENTAL

2.1. Materials

The monomers, *N*-vinylpyrrolidone (VP, Merck) and vinyl acetate (VA, Merck) were used no-distilled. 2,2-azobisisobutyronitrile (AIBN, Aldrich) was re-crystallized from methanol. The solutions, ethanol (Merck), Diethyl ether (Merck), were used as received.

2.2. Measurements

2.2.1. Analysis methods

FTIR spectra of the copolymers were recorded with FTIR Nicolet 410 on KBr pellets by a 4000 - 400 cm^{-1} range spectrometer. Differential Scanning Calorimetry (DSC) graphs of the copolymers were recorded with Shimadzu TA-60 Equipment. Mass distributions and molar masses of copolymers were determined by GPC method on liquid chromatography system (Shimadzu), LC-10AD-VP pump, RID-10A detector, SPD-10A-VP.

2.2.2. Copolymerization

Mixtures of monomers VP, VA and ethanol were loaded into glass flask connected with agitator, reflux equipment and temperature controlled by water bath. During the reaction, the oxygen is removed by nitrogen gas. After raising the temperature to the reaction temperature, AIBN was loaded and the reaction was started.

The reaction mixture was poured into 600 ml of diethyl ether to precipitate the product, the product is filtered and dissolved in 50 ml of ethanol and precipitated in 600 ml of diethyl ether. This process was repeated 3 times. Final product was vacuum dried at 60 °C to constant weight.

2.2.3. Conversion determination

To determine the conversion, after a certain period of time, shall take the reaction solution, cooled to room temperature and the product precipitated in excess diethyl ether. The precipitate was dissolved in ethanol and further precipitated in diethyl ether, this process was repeated 3 times. Then the product was filtered and dried under vacuum to constant weight. Conversion is calculated by the formula (1):

$$H = \frac{m}{m_o} \times 100 \% \quad (1)$$

where: H – conversion of monomer (%), m - product weight (g); m_o - monomer initial weight (g).

3. RESULTS AND DISCUSSION

3.1. Effect of temperature and time on monomer conversion into copolymer

To study the effects of temperature, reaction time on the copolymerization, the reaction is carried out with the following conditions: monomer concentration of 40 % compared to the

volume of solvent, concentration of initiator (AIBN) 1,5 % of the total volume of monomer solution, reaction temperature ranging from 60 to 75 °C. The results are presented in figure 1.

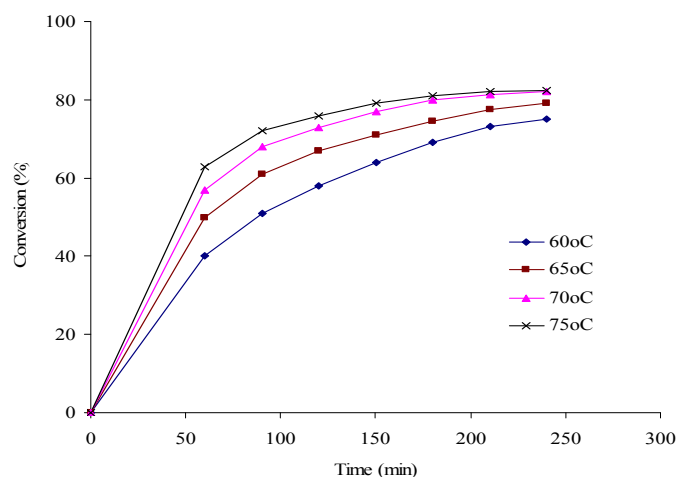


Figure 1. Effect of temperature and reaction time on conversion.

The results in figure 1 show that the reaction temperature increases, the conversion of monomer increases. The reaction time increases rapidly in the first 50 minutes, increasing slowly in the next period and reached a stable level after 250 minute reaction. When the reaction temperature increases, the speed of all chemical reactions is increased, including base reactions during polymerization. The increase in the speed of reaction leads to the formation of active centers and increase conversion monomers into copolymers. When the temperature is raised, the monomer conversion ratio is increased. At 70 °C , the monomer conversion increased in the first 50 minutes, an increase in the next period and remained stable after 240 minutes reaction. The conversion reach the highest level at 240-minute reaction, in value 82,4 %.

3.2. Effect of initiator concentration on conversion of monomer into copolymer

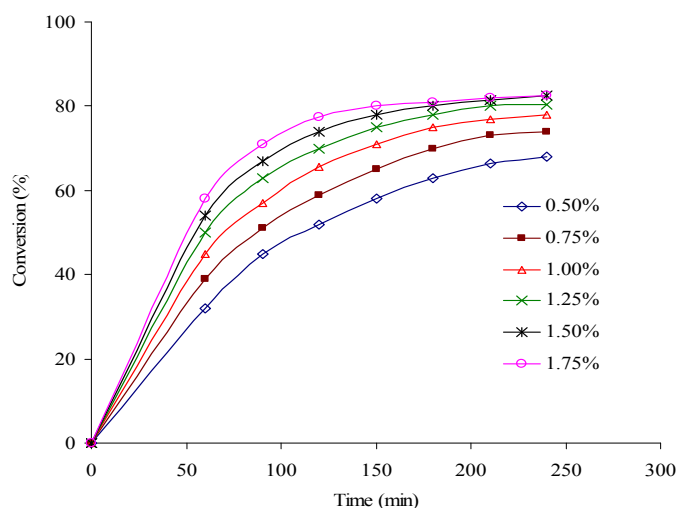


Figure 2. Effect of concentration initiator on monomer conversion into copolymer.

In order to study the effect of initiator concentration, reaction was carried out under the following conditions: 70 °C reaction temperature, monomer concentration 40 % compared with the solvent, initiator concentrations ranged from 0,5 to 1,75 %. Results are presented in figure 2.

Results figure 2 shows, the amount of initiator affects conversion ratio, the copolymerization reaction occurs by free radical mechanism, triggered substances directly affect the copolymerization. As the concentration initiator is increased leading to increased chain development, increased conversion ratio, besides leading to reduced chain lengths, molecular weight copolymers decreased. The conversion reached the highest value at 1,5 % initiator (w/w) when the reaction time of 240 minutes.

3.3. Effect of monomer concentration on monomer conversion into copolymer

To study the effect of monomer concentration on performance polymerization reaction, the reaction was carried out at 70 °C, the amount of initiator 1.5 % (w/w), monomer concentration changes from 30 to 45 %. Results are presented in figure 3.

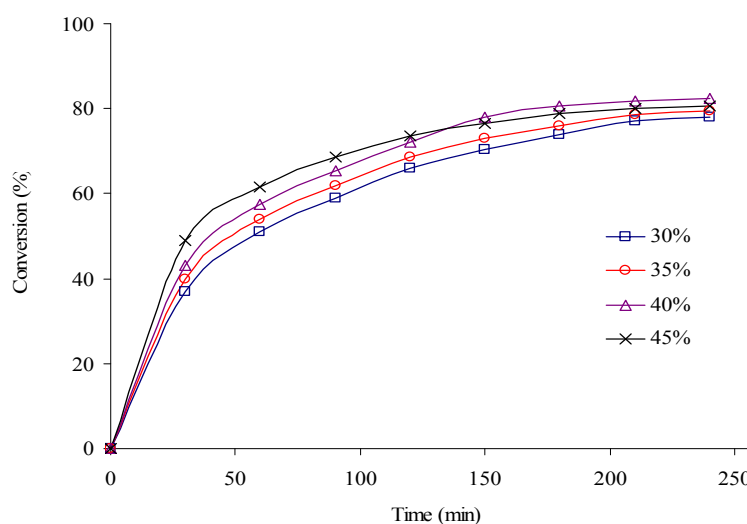


Figure 3. Effect of monomer concentration on the conversion yield to VP-co-VA copolymer.

Figure 3 shows the results at 30 % concentration of initial conversion rate increases slowly, prolonging the conversion rate increases to a constant value, at the time of 240 minutes, when the monomer concentration increased to 45 %, the conversion rate increased in the first period, and prolonged reaction time, the metabolic rate increases until a constant value at the time of 240 minutes. However, in 45 % monomer (w/w), conversion increased suddenly in period of first 45 minutes. After a period of 240 minutes, conversion monomer into copolymer reached highest value at 82,4 %, in 40 % monomer (w/w).

3.4. Molecular weight measurement of VP/VA copolymer

The GPC was done to determine the molecular weight of the VP/VA copolymer. The result describes in figure 4.

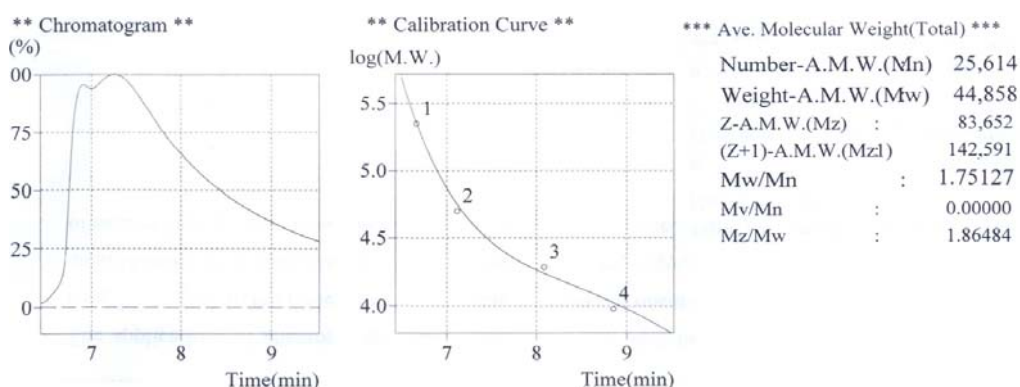


Figure 4. The GPC spectral chromatograms of VP/VA copolymer.

Figure 4 shows that, the average molecular weight of the copolymers obtained are $M_w = 51000$ (g/mol) with polymer dispersion index $PD = 1,791$. The result shows molecular weight distribution relative characteristics.

3.5. FTIR spectra of VP/VA copolymer

The composition of copolymer can be determined by FTIR. The result is described in figure 5.

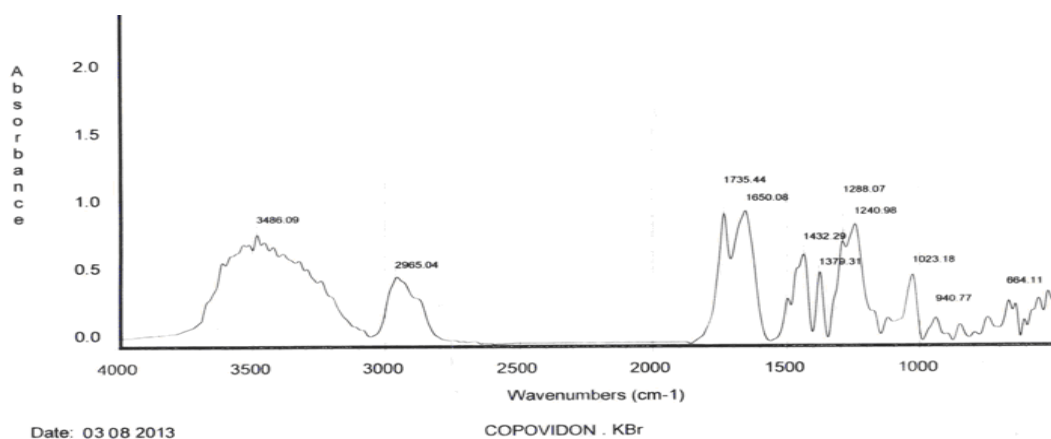


Figure 5. FTIR spectra of VP/VA copolymer.

Figure 5 demonstrates that, in contrast to the spectrum of poly(*N*-vinyl pyrrolidone) homopolymer (PVP), a characteristic peak appears around 1735 cm^{-1} . Meanwhile, the asymmetric stretches C-O-C were seen at 1240 cm^{-1} . The C-N stretching absorption appears at 1288 cm^{-1} . This is at higher frequency than the corresponding absorption of normal aliphatic amine because the force constant of the C-N bond is increased by resonance with the ring C=O groups (ring of VP). The FTIR of VP/VA copolymer also shows that the C=C stretching absorption don't appear at 1624 cm^{-1} (characteristic of monomers), this proves the copolymers no residual monomers.

3.6. Differential Scanning Calorimetry analysis (DSC)

DSC curves of PVA, PVP, and VP/VA copolymer are given in figure 6.

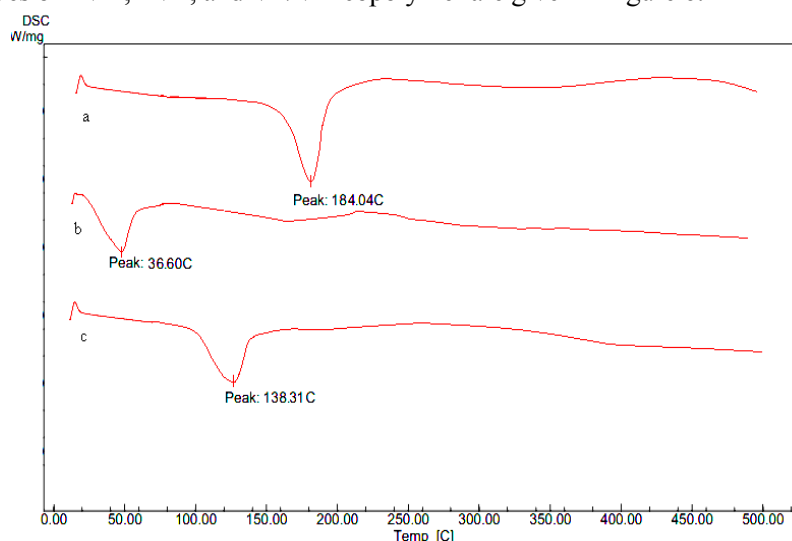


Figure 6. DSC curves of PVP homopolymer (a); PVA homopolymer (b); VP/VA copolymer (c).

Figure 6 shows that, curve DSC of VP/VA copolymer (figure 6 (c)) only appears on Tg, Tg values of copolymer lie between Tg values of PVP and PVA. In addition, peak Tg of PVA is significantly clear, this demonstrates the molecular weight distributions of VP/VA copolymer is relatively uniform.

4. CONCLUSION

VP/VA copolymers were prepared through the free radical copolymerization in ethanol solutions, using AIBN as an initiator.

Optimal conditions of copolymerization: 70 °C reaction temperature, reaction time 240 min, concentration of 1,5 % initiator, monomer concentration 40 %. With this condition, the copolymers are metabolized forming 82,4 %, average molecular weight of the copolymers obtained are Mw = 51000 (g / mol) with polymer dispersion index PD = 1,791.

Characteristics of VP/VA copolymer were studied by IR spectra, DSC analysis and GPC method.

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TÓM TẮT

TỔNG HỢP VÀ TÍNH CHẤT CỦA POLY (N-VINYL PYROLIDON-co-VINYL AXETAT)

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Copolymer của n-vinyl pyrrolidone (VP) và vinyl axetat được tổng hợp bằng phương pháp trùng hợp gốc tự do sử dụng chất khơi mào 2,2-azobisisobutyronitril. Tính chất của copolymer được xác định bằng phổ hồng ngoại (IR), phân tích nhiệt vi sai quét (DSC), thẩm thấu gel (GPC). Ảnh hưởng của nhiệt độ, nồng độ monomer và nồng độ chất khơi mào đến độ chuyển hóa của copolymer đã được nghiên cứu. Điều kiện tối ưu để monome chuyển hóa thành copolymer là: nhiệt độ phản ứng: 70 °C, nồng độ monome: 40 %, nồng độ chất khơi mào: 1,5 % (theo khối lượng monome) và thời gian phản ứng 250 phút.

Từ khóa: copolymer, N-vinyl pyrrolidone, vinyl axetat, trùng hợp.