Investigation of Reaction Conditions for Preparation of Medium Molecular Weight Poly(vinyl alcohol) as Emulsifier

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A B S T R A C T

Poly(vinyl alcohol) (PVA) is a water soluble polymer with excellent physical and chemical properties. The basic properties of this polymer depend on its molecular weight, degree of hydrolysis and distribution. Since the commercial applications of PVA are many and varied, therefore, a special grade of PVA with considerable properties is required as an emulsifier. A polymerized ester can be used for preparation of PVA types, because vinylalcohol monomer does not exist in the free state. The characteristics of the preparation of poly(vinyl acetate) (PVAc) are very important in the manufacture of PVA. In this work, a partially hydrolyzed grade of PVA having characteristics suitable for application in emulsion polymerization of vinyl acetate (VAc) ($\overline{M}_v$: 77200, hydrolysis degree: 89.2%) was prepared by investigation of reaction conditions for solution polymerization of VAc by the aids of α,α' azobisisobutyronitrile (AIBN) initiator in methanol and the subsequent saponification reaction of the resulted PVAc in the presence of NaOH. This was including investigation of the effect of [VAc]/[AIBN] ratio and polymerization time for preparation of PVAc at 60ºC in terms of VAc conversion and PVAc molecular weight, then the effect of saponification time of PVAc in terms of the molecular weight and hydrolysis degree of PVA product. In case of some samples, concentration of the monomer relative to that of the initiator plays an important role in VAc conversion value and controlling the PVAc molecular weight. The results from saponification of PVAc samples revealed that, only one of the samples was that its saponification resulted in PVA material desired molecular weight at 1 h. ^{1}H NMR Spectra of PVAc and PVA were used to show a branched molecular structure of PVAc and estimation of the degree of hydrolysis of a PVA sample. The presence of typical characteristics absorption bands in IR spectra of PVAc and PVA samples agrees with proposed structures. To confirm the result earned, the characteristics of PVA obtained were compared with those of the commercially used PVA grades (Mowiols).

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a polymer with unique physical and chemical properties. Since its discovery in 1915 by Klatte [1], it has found many applications and new areas are still being added.

The polymer properties include; solubility in water, the specific colloidal characteristic of aqueous solution, film formation and reactivity of the numerical hydroxyl groups with other substances such

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as reactive resins, and aldehyde, etc. Commercially, PVA is manufactured mainly through saponification of poly(vinyl acetate) (PVAc), but it is also produced from other polyvinyl esters and polyvinyl ethers [2-10].

As the special properties of a PVA eg., degree of hydrolysis (degree of saponification or acetyl group content), average molecular weight and distribution of residual acetyl groups sequences provide an individual property profile, a variety of PVA grades is produced for various applications. These range from partially hydrolyzed (87-89%) to a fully hydrolyzed (97.5-99.5%) degree.

The most common grades of PVA in each area of applications, either fully or partially hydrolyzed have polymerization degree of 1700 [2]. Today, much of partially hydrolysis PVA produced is used as a protective colloid in manufacturing of polymer emulsions. PVA grades with average molecular weight of 78000 and hydrolysis degree of 87-89% are the predominant and often the only polymer type which is used for emulsion polymerization of vinyl acetate (VAc) monomer [11]. This additive keeps the monomer being polymerized in ultra-fine of dispersion during production of the emulsion and stabilizes the finished

PVAc emulsion against coagulation during mechanical stress as well as freezing [12-14].

The aim of the present work was to study the reaction conditions for preparation of a PVA grade with a special molecular weight and degree of polymerization as an emulsifier which is widely used in manufacturing of PVAc emulsions, also is not disclosed in the published literature.

EXPERIMENTAL

Materials

Vinyl acetate (VAc) monomer (>99% purity) was purchased from Arak Petrochemical Industries of Iran. Methanol (MeOH), α,α' azobisisobutyronitril (AIBN), acetic acid 60%, sodium hydroxide (mp 318ºC) purchased from Merck Co. were used without further purification.

In this study a number of commercial PVA grades (Hoechst Co.) with the characteristics shown in Table 1 were used as standards samples.

Polymerization of Vinyl Acetate

The polymerization of vinyl acetate (VAc) was per-

Table 1. Characteristics data of a number of commercial PVA grades (Mowiol types) used as standard samples.

PVA	Viscosity	Degree of hydrolysis	Residual acetyl	Maximum ash
Partially saponified grades	(MPa.s)	(mol%)	group (wt%)	(%)
Mowiol 4-88 N38	4 ± 0.5	87.7 ± 1.0	10.7 ± 0.7	<0.5
Mowiol 8-88 N58	8 ± 1.0	87.7 ± 1.0	10.7 ± 0.7	<0.5
Mowiol 18-88 N78	18 ± 1.5	87.7 ± 1.0	10.7 ± 0.7	<0.5
Mowiol 26-88	26 ± 1.5	87.7 ± 1.0	10.7 ± 0.7	<0.5
Mowiol 30-92	30 ± 20	92.4 ± 0.9	6.9 ± 0.7	
Mowiol 40-88 N88	40 ± 20	87.7 ± 1.0	10.7 ± 0.7	<0.5
Fully saponified grades				
Mowiol 4-98 N39	4 ± 1.0	98.4 ± 0.4	1.5 ± 0.4	<0.5
Mowiol 0-98	10 ± 1.0	98.4 ± 10.4	1.5 ± 0.4	<0.5
Mowiol 20-98	20 ± 1.5	98.4 ± 0.4	1.5 ± 0.4	<0.5
Mowiol 26-99 N79	28 ± 2.0	99.4 ± 0.4	0.5 ± 0.4	<0
Mowiol 56-98	66 ± 4.0	98.4 ± 0.4	1.5 ± 0.4	<1.0
Mowiol 66-100	66 ± 4.0	98.7 ± 0.8	0.4 ± 0.2	<1

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Table 2. Conditions and results of the solution polymerization of VAc at 60ºC.

| Sample no.	VAc (g)	MeOH (g)	AIBN (g)	VAC Conversion (%)	Polymerization time (h)	M_V of PVAc
1	100	150	0.1	25	2	-
2	100	150	0.1	44	3	11000
3	100	150	0.1	49	4	-
4	100	150	0.1	61.5	5	47463
5	100	150	0.1	66	6.5	52100
6	200	200	0.3	50.05	2	84505
7	267	133	0.3	55	2	169327
8	300	100	0.3	66	2	222540
9	300	100	0.75	-	4	-
10	300	100	0.375	67	4	172990
11	300	100	0.5	63	4	193613
12	300	100	0.75	60	2	215156
13	300	100	0.75	62	3	268906

formed in a pyrex round-bottle glass immersed in an electrical bath equipped with a mechanical stirrer (600 rpm), reflux column, nitrogen bleed and a dropping funnel. First, definite amounts of VAc and methanol were transferred into the reactor and its temperature was let to rise up and fix at 60ºC under reflux and passage of slow stream of nitrogen gas. Then, AIBN was added to the solution. After a definite period of time, the hot bath was changed to cold water bath for stopping the reaction. The resulting product (PVAc) was filtered and purified by washing with plenty of distilled water for several times, then it was dried in a

vacuum oven at 50ºC for 24 h. The VAc conversion was calculated on the basis of the resulting PVAc weight.

The polymerization conditions and results obtained are summarized in Table 2, and variation of VAc conversion as a function of the polymerization time is shown in Figure 1.
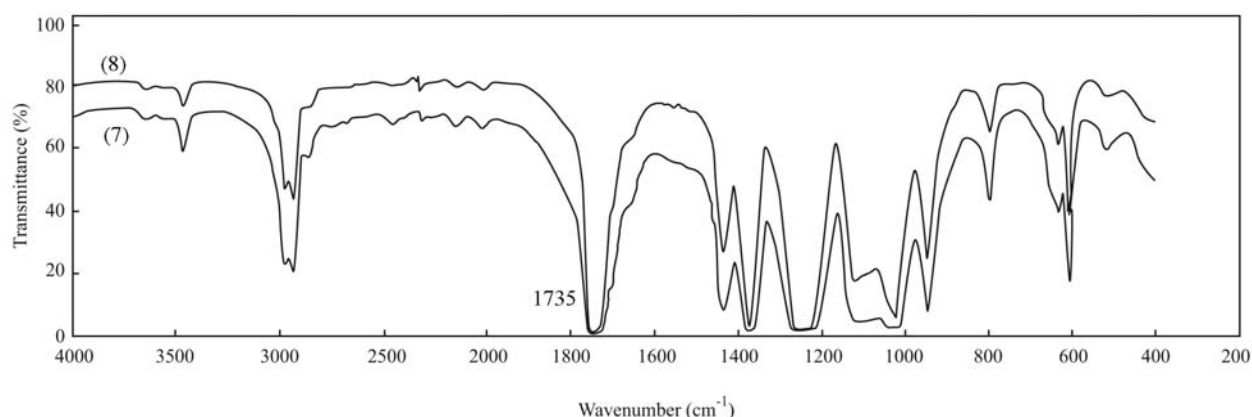
Saponification of PVAc
Definite amount (~110 g) of PVAc sample (No.8) was dissolved in 400 mL methanol and then treated with a definite volume of 40% solution of NaOH in methanol at 35ºC under a continuous stirring (500 rpm) at different lengths times (Table 3). Following to
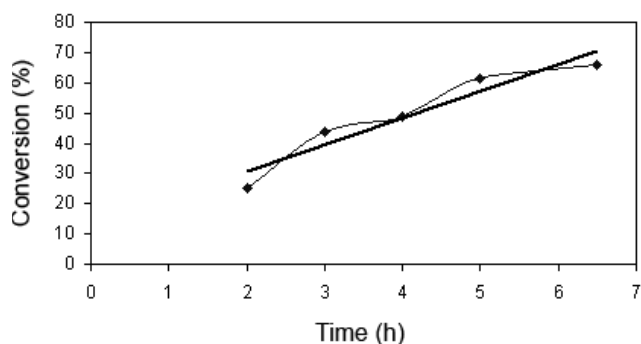
Figure 1. Variation of VAc conversion in terms of the polymerization time (T=60ºC, AIBN=0.1 g).

Table 3. The effect of saponification time on properties of the resulted PVA from PVAc No 8.

Sample no.	Time (min)	M_v of PVA	Degree of hydrolysis (mol%)
1	20	65820	82.4
2	40	68900	85.2
3	60	77200	89.2
4	75	79000	92.5
5	90	83000	93.8

Figure 2. IR Spectra of the synthesized PVAc samples 7 and 8.

this, the solution was neutralized with a 60% solution of acetic acid in water to stop the saponification reaction. The resulted PVA sample was filtered and washed well with plenty of methanol and dried at 60ºC in an oven for 12 h. The reaction conversion was calculated by measuring the weight of PVA (56%).

Characterization of the Prepared Samples

The molecular weight of PVAc and PVA were determined by solution viscometry (JIS K6726) [1]. This was conducted on (<1%) solutions of PVAc in methanol and (<1%) solutions of PVA in water at 30ºC and 25ºC, respectively, using an Ubbelohde capillary viscometer and Mark-Houwink equations [15]:

$$[\eta] = 31.4 \times 10^{-5} \left[M_v \right]^{0.6}_{(PVAc)} \tag{1}$$

$$[\eta] = 73.1 \times 10^{-5} \left[M_v \right]^{0.616}_{(PVA)} \tag{2}$$

where $[\eta]$ represents intrinsic viscosity of PVAc and PVA samples in terms of dL/g and M_v represents viscosity-average molecular weight of the polymer samples.

Table 4. Characteristics of synthesized PVA sample.

Properties	Amount
M_v	77200
DP	1618
Volatile component (%)	4
pH of a solution of 4% concentration	5
Viscosity (cp) of a solution of 4% concentration	17.6
Acetyl residue (%)	10.8
Ash content (%)	0.1

Determination of hydrolysis degree of PVA samples also was made using JIS K6726 standard method. According to this method, dried sample (~1 g) was dissolved in a solution (40 mL) of 1:3V/V MeOH/distilled water. After addition of 50 mL aqueous solution of 0.1 N KOH, it was refluxed for 2 h, under continuous stirring (500 rpm) to hydrolyze residual acetate groups on the polymer chains. The moles of potassium hydroxide consumed are equivalent to the number of hydrolyzable acetate groups and are determined by back titration with an aqueous strong solution of 0.1 N HCl.

The degree of hydrolysis is calculated from this number and the initial sample weight [1]:

$$\text{Degree of hydrolysis} = 100 - \frac{0.43(a - b)}{m \times p} \tag{3}$$

where m, b, a, and p are the initial sample weight, the volume of HCl consumed for blank, the volume of HCl consumed for sample, and the sample pure component (solid content), respectively.
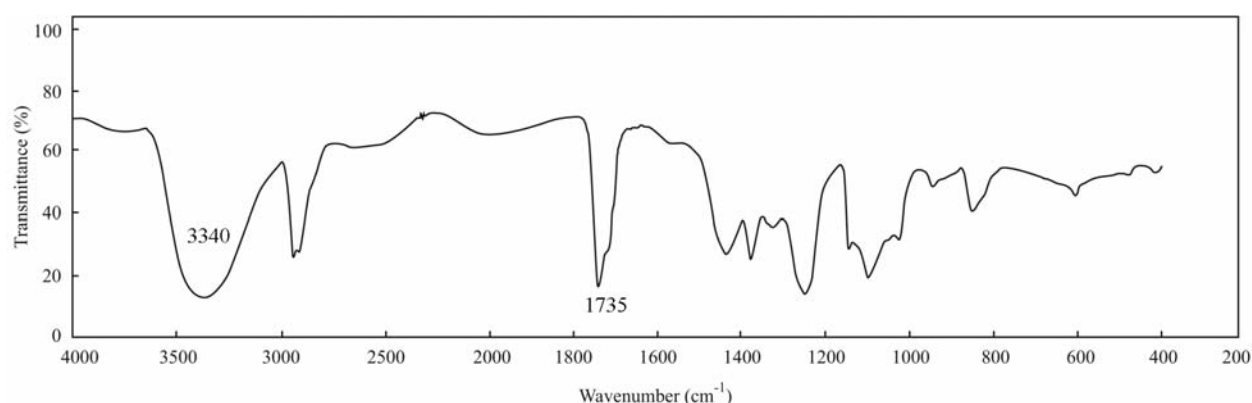
The characterization also included the measuring of the pH and viscosity of a 4% aqueous solution of each sample by digital pH Meter (P.M.T. Model 2002) and a Hoppler falling-ball viscometer (Haake Co., UND53015 model).

The characteristics of one of the PVA samples are given in Table 4. The branching degree is determined by ^{1}H NMR spectroscopy in D_2O and $CDCl_3$ using Jeol FX90 model and measuring the intensity ratios of methyl/methylene proton signals.

FTIR Spectra of PVAc and PVA samples were also obtained for comparison purposes with the commer-

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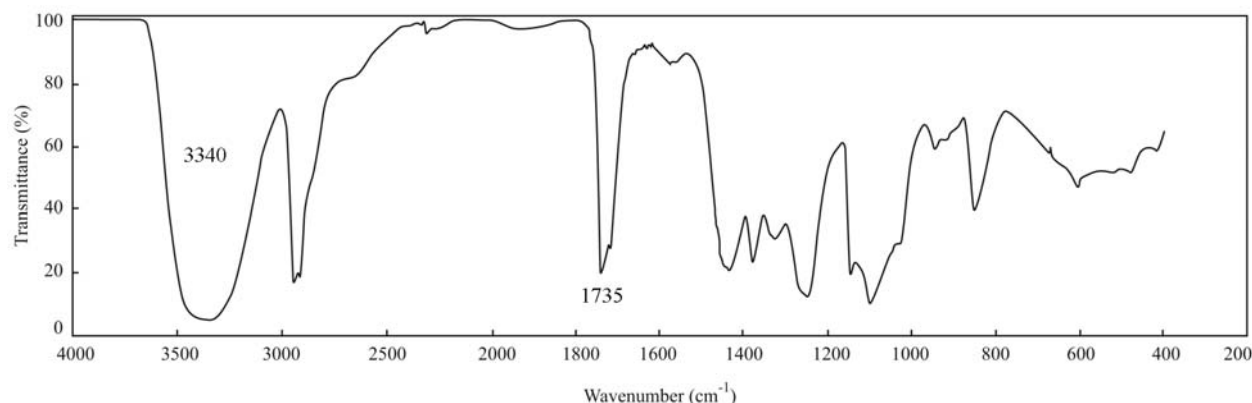
Figure 3. IR Spectrum of a partially hydrolyzed synthesized PVA.

Figure 4. IR Spectrum of a commercial partially hydrolyzed PVA; N78.

cial PVA grades using a Perkin-Elmer IR spectrometer 2000 [16].

RESULTS AND DISCUSSION

According to free radical polymerization process the rate of polymerization of monomer is increased as the efficiency and concentration of radical forming initiator and monomer are increased. Industrially the most important objective is reducing the monomer residual concentration, increasing the output of polymerization and controlling the molecular weight of the resulted polymer for a desired quality [17,19].

The quality of a resulting PVAc from radical polymerization of VAc depends on factors such as type and amount of initiator and solvent used, polymerization time at constant temperature and the percentage of monomer conversion.

The type of solvent affects not only the average molecular weight of PVAc and final PVA product but also the nature of the polymer chain end groups [20].

Figure 1 shows monomer conversion as a function of reaction time. It can be observed from this figure that conversion increases with the reaction time for the five reactions and reaches a constant value of 66%. Furthermore, with increasing the initiator or monomer concentration, conversion increases as well. As a result, higher conversion was obtained in a shorter time by increasing the initiator or monomer concentration. This is in accordance with the results observed in Table 2 in which increasing initiator or monomer concentration decreases the reaction times.

Table 5. FTIR Peak identification of PVAc and PVA [2,23].

Description	Peak location (cm^{-1})
OH	3340
CH$_2$	2942
CH	2840
C=O	1735, 1260
Tacticity of PVA	916
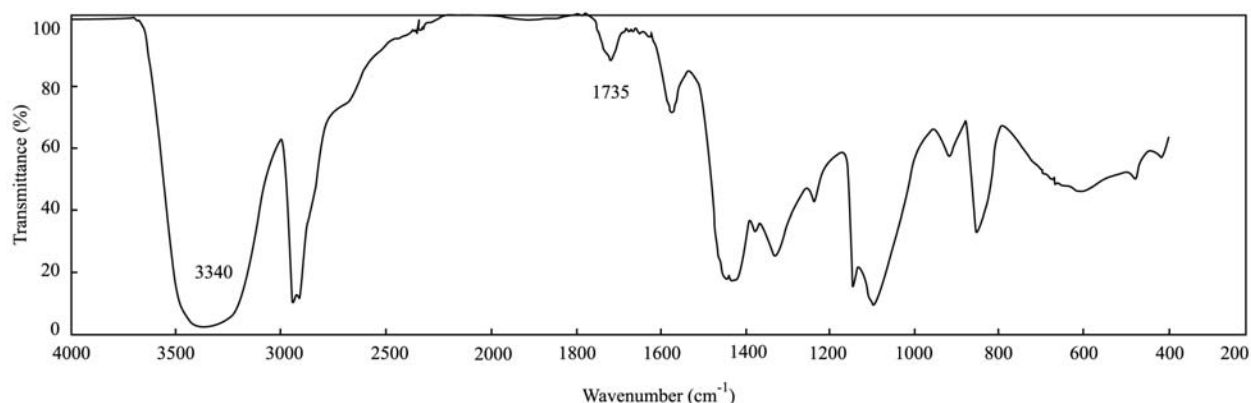
Figure 5. IR Spectrum of a commercial fully hydrolyzed PVA; N79.

By increasing the monomer concentration, the conversion is increased (in case of sample 8) as a result of attacking more number of radicals generated from the initiator to the monomer double bond with high electron density.

Controlling solution polymerization of VAc becomes more difficult by using a high concentration of VAc due to autoacceleration of the reactions which lead to excessive chain transfer during polymerization [11], but autoacceleration is not performed at low temperature [21,22]

According to theoretical prediction, M_v of PVAc and PVA should be generally increased with decreasing the initiator concentration or decreasing the polymerization temperature. This was clearly observed in the case of sample 9 in Table 2, as its polymerization occurred so fast that the mixer stopped from rotating.

Increasing the AIBN concentration results in an increase in the polymerization rate as it is shown in samples 9-11 of Table 2.

As it is observed in case of samples 6-8, concentration of the monomer relative to that of the initiator plays an important role in VAc conversion value and molecular weight control of PVAc.

The molecular weight of PVAc has been increased to 222,000 for sample 8 which is almost twice that of sample 6. By increasing the initiator concentration the rate of VAc polymerization is increased and monomer polymerization proceeds faster.

According to Table 2, the results from saponification of PVAc 8-12 are revealed that, sample 8 was the only one which its saponification resulted in PVA material with desired molecular weight (77200) within l h. The effect of the saponification time for the
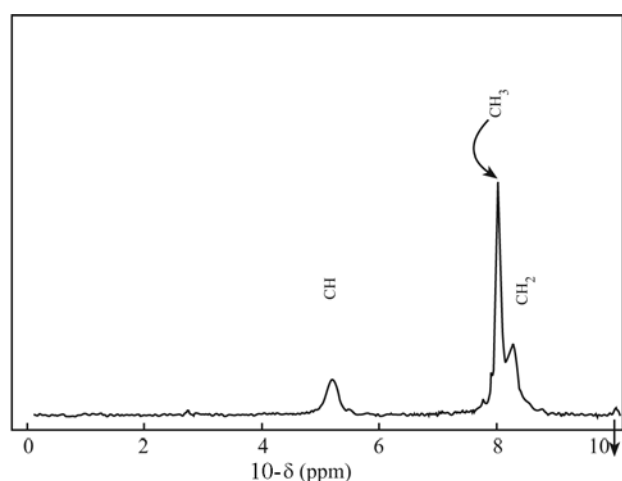
Figure 6. ¹H NMR Spectrum of the synthesized PVAc; sample 8.
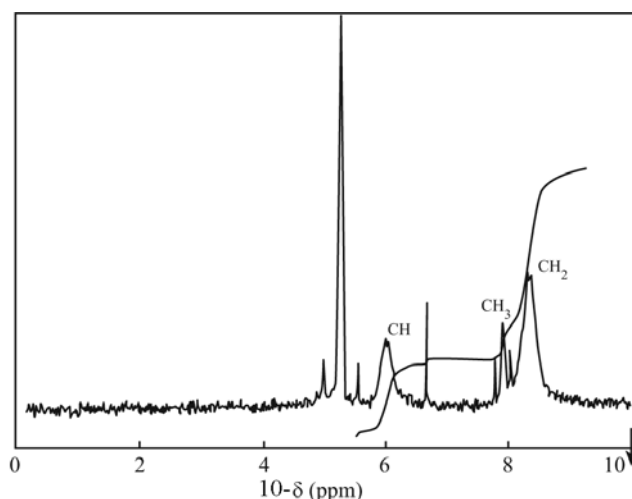
**Figure 7.** ¹H NMR Spectrum of a synthesized partially hydrolyzed PVA.
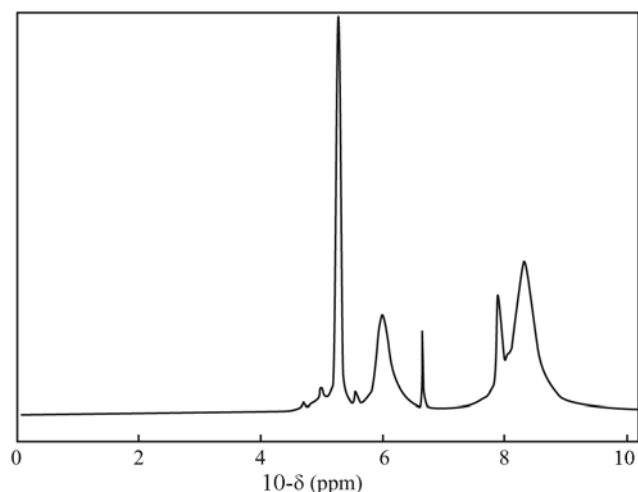
Figure 8. ^{1}H NMR Spectrum of the commercial partially hydrolyzed PVA; N78.

PVA sample, the PVA molecular weight and degree of hydrolysis are presented in Table 3 and characteristics of synthesized PVA sample are shown in Table 4.

The difference between molecular weight of this PVA and its PVAc mostly stems from branched structure of the latter which is broken down in saponification step. Branching of PVAc is increased with increasing VAc conversion and the polymerization temperature, through chain transfer reactions.

IR Spectra of PVAc samples 7,8 and the resulting PVA sample are presented in Figures 2 and 3. The presence of typical characteristic absorption bands at 1735 cm^{-1} (due to carbonyl groups stretching) and 3340 cm^{-1} (due to hydroxyl bond stretching) in the
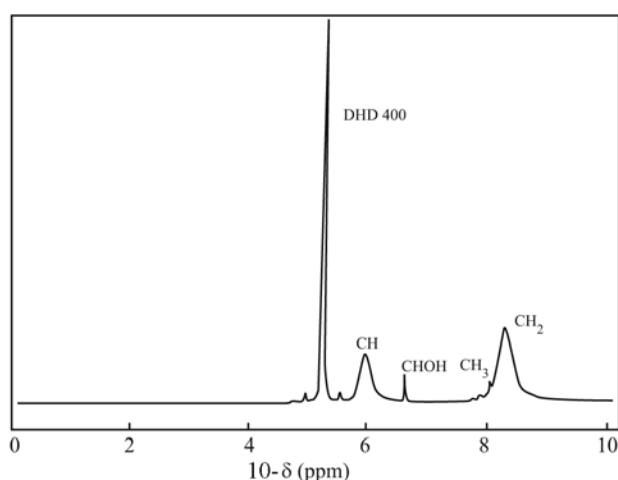
Figure 9. ^{1}H NMR Spctrum of the commercial fully hydrolyzed PVA; N79.

Table 6. Assignment of ^{1}H NMR in PVAc and PVA [2].

Assignment	10-δ (ppm)
CH$_2$	8.20
CH$_3$	7.98
CH	5.08
DHO	4.80
CH (PVA)	6.00
CH$_3$ (PVA)	6.90
CH$_2$ (PVA)	8.30

spectra confirms the presentation of PVAc and PVA (Table 5). IR Spectra of a partially and fully hydrolyzed commercial PVA are shown in Figures 4 and 5. Figure 4 shows an absorption band, 1735 cm^{-1} due to presence of acetate groups' concentration in comparison with Figure 5. IR Spectrum of synthesized PVA sample in Figure 3 is quite similar with that of a commercial partially hydrolyzed PVA sample (N78) in Figure 4.

By comparing the molecular weights of PVAc and PVA samples, it is deduced that former sample has a branched molecular structures mostly on CH$_3$ of acetyl groups which may by broken down during saponification. According to eqn (5), the degree of branching (DB) for the acetyl group of PVAc was calculated as follows [20]:

$$DB = \frac{DP_1}{DP_2} - 1 \qquad (5)$$

where DP$_1$ is the degree of polymerization of PVAc and DP$_2$ is the degree of polymerization of PVA.

DB= 2587/1755 -1= 0.47

As a rule, the difference between degree of polymerization of PVAc and PVA is mostly due to branched structures which may be broken down when saponified.

^{1}H NMR Spectrum of PVAc sample 8 represents signals at chemical shifts of 8.2, 7.98 and 5.08 ppm indicating the presence of CH$_2$, CH$_3$ and CH groups, respectively, with a proton ratio of 2:2.6:0.6 which is very close to the theoretical ratio (2:3:1) for PVAc. Therefore, it may be concluded that PVAc sample 8 synthesized in this work is branched at CH$_3$ and CH positions which are not disappeared on saponification.

^{1}H NMR Spectrum of the synthesized PVA sample

is compared with those of two types of commercial PVA samples in Figures 7-9. As the OH protons present in the molecules of PVA can exchange with deuterium atoms of D_2O solvent for ^1H NMR spectroscopy used, the OH signal is disappeared in the spectra and proton signal due to DHO is appeared at 4.8 ppm. The signal area due to CH_3 relative to that of CH_2 could be used for estimation of the degree of hydrolysis of a PVA sample. As much as this ratio is increased the degree of hydrolysis of a PVA is lower (Table 6).

For a fully hydrolyzed PVA the signal due to CH_3 is not appeared. The signals areas ratio of $CH:CH_2$ is equal to 2.5:1 for PVA sample which is almost in comparison with the theory of value 2:1 which confirms the branching of the PVA.

CONCLUSION

PVA Emulsifier with a desired degree of hydrolysis (89.2%) and molecular weight (~78000) was synthesized through radical solution polymerization of VAc in methanol at 60ºC followed by saponification of the resulting PVAc. This was accomplished by optimizing the starting materials (VAc, AIBN, MeOH) ratio for the synthesis of PVAc and concentration of NaOH and the period of time for the saponification of PVAc.

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