Development of a Nonaqueous Solvent System for Poly(vinyl alcohol) and Its Characterization

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Received 12 October 1998; accepted 8 March 1999

ABSTRACT: Solubility of poly(vinyl alcohol) (PVA) in water prevents the preparation of various derivatives through homogeneous techniques as most of the derivatives thus formed are insoluble in aqueous medium. There are a number of solvents that can swell PVA under hot conditions but cannot dissolve PVA. In the present study, *N*,*N*-dimethyl acetamide (DMAc) has been identified as solvent in which PVA can be dissolved in the presence of an equimolar amount of lithium chloride (LiCl). ¹H nuclear magnetic resonance (¹H-NMR), ¹³C-NMR, infrared (IR), and X-ray diffraction (XRD) studies have been carried out to characterize the regenerated poly(vinyl alcohol) (RPVA). DMAc-LiCl is found to be a true solvent system for dissolution of PVA. An attempt has also been made to prepare poly(vinyl acetate) from this solution of PVA by a homogeneous technique. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 663–669, 1999

Key words: poly(vinyl alcohol); *N*,*N*-dimethyl acetamide–LiCl; crystallinity; crystal structure; poly(vinyl acetate); activation energy

INTRODUCTION

Over the last decade, there has been increased interest in developing organic solvent systems for poly(vinyl alcohol) (PVA). Due to strong inter- and intramolecular hydrogen bonding, PVA is insoluble in organic solvents. So far, water is the only the known solvent for PVA.¹ Some derivatives like esters or acetals of PVA are difficult to prepare in aqueous medium because the maximum extent of acetalization cannot be achieved.^{2,3} Therefore, development of an organic solvent system for PVA may have significant commercial potential. Recently, a class of catalysts, such as $C_2H_5ONO_2.DMSO$, $C_2H_5CI.DMSO$, $C_2H_5Br.DMSO$, $C_2H_5I.DMSO$, $C_2H_5OSO_3H.DMSO$, $C_2H_5OPO_3H_2.DMSO$, and $C_2H_5BF_4$. DMSO, have been identified in presence of which PVA can be dissolved in solvents like *N*,*N*-dimethyl formamide.⁴ A number of poly vinyl esters and acetals have also been prepared from PVA.^{5,6}

In this study, we explored the possibility of dissolving PVA in an organic solvent system without catalyst, and we found that N,N-dimethyl acetamide/lithium chloride (DMAc–LiCl) could be use as a solvent system for PVA; the maximum solubility of PVA was found to be 6.7% without any gel formation, which was more than what reported with catalyst system.⁴ It was also observed that during the dissolution process though there was a change in the crystal structure of PVA, the chemically active centers remained intact. No degradation or crosslinking in the polymer chain was noticed.

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Journal of Applied Polymer Science, Vol. 74, 663-669 (1999)

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Figure 1 ¹³C-NMR spectra of 0.02/0.02/0.96 PVA–LiCl–DMAc.

EXPERIMENTAL

Materials

PVA, white crystalline forms (s.d. fines; viscosity average molecular weights of 14,000 and 1,25,000), DMAc (s.d. fines) LiCl (CDH), acetone (CDH), pyridine (CDH), acetic anhydride (E-Merck), and acetyl chloride (E-Merck) were used without further purification.

Methods

Dissolution of PVA and Regeneration

4.4 g (0.1 mol) of PVA was dissolved in 440 mL (4.75 mol) of DMAc in presence of 4.25 g (0.1 mol) LiCl at 40°C with constant stirring for 3 h to get 1% (w/v) solution. From a part of the solution, PVA was regenerated using acetone as a nonsolvent. For complete removal of LiCl from regenerated poly(vinyl alcohol) (RPVA), it was successively dissolved in water and then regenerated with acetone until complete removal of LiCl from RPVA and was confirmed by atomic absorption spectroscopy.

Table IEffect of Added LiCl and PVA on ¹³C-NMR Chemical Shift (ppm) of DMAc

DMAc	DMAc-LiCl	PVA-DMAc-LiCl
168.93 36.73 33.65 20.53	$\begin{array}{c} 170.61 \ (-1.68) \\ 37.60 \ (-0.87) \\ 34.40 \ (-0.75) \\ 21.02 \ (-0.49) \end{array}$	$173.04 (-4.11) \\38.48 (-1.75) \\35.45 (-1.8) \\21.81 (-1.280)$



Acetylation Reaction

100 mL each of PVA 1% (w/v) solutions (0.023 mol, based on one monomer unit) were taken in two reaction vessels separately. To one, 1.8 mL (~ 0.023 mol) pyridine was added, followed by dropwise addition of 2.2 mL (~ 0.023 mol) acetic anhydride. Acetylation was carried out at 50°C for 5.5 h. To the other reaction vessel, 1.8 mL (~ 0.023 mol) of acetyl chloride was added without any catalyst, and acetylation was carried out at 40°C for 1 h. The products were then isolated by pouring the reaction mixtures separately into 1 L each of cold distilled water and filtered and Sohxlet-extracted in water for 8 h.

Determination of Degree of Substitution

The average degree of substitutions (DS) and acetyl contents (%) for poly(vinyl acetates) prepared by reaction with anhydride $[PVAc_{(anh)}]$ and acetyl chloride $(PVAc_{(Cl)})$ were then determined by saponification method following the Ebrstadt procedure.⁷

Intrinsic viscosities and molecular weights of PVA, RPVA, $PVAc_{(anh)}$, and $PVAc_{(Cl)}$ were found out viscometrically at 25°C using water as a solvent for PVA and RPVA and acetone for polyvinyl acetates.⁸ The infrared (IR) spectra were recorded in a Perkin-Elmer model 580 B spectrometer using thin films of the samples. Both ¹H nuclear magnetic resonance (¹H-NMR) and ¹³C-NMR spectra were taken in a 300-MHz NMR spectrometer for PVA and RPVA using D₂O as solvent. The ¹³C-NMR spectra of PVA–DMAc–LiCl was also taken, and chemical shifts were determined relative to tetramethylsilane (TMS). X-ray diffraction (XRD) data were collected using a computer-controlled X-ray diffractometer (Type, JDX-11P3A, JEOL, Japan) with pulse-height analyzer and a scintillation counter. The measuring conditions were as follows: mode, step; KV, 40; start angle,



Figure 2 ¹³C-NMR spectra of (a) PVA and (b) RPVA.

2°; target, Cu; mA, 20; stop angle 60°; measuring time, 0.5 s; step angle, 0.05.

The degree of crystallinity (K_c) was found out using the following equation⁹:

$$K_c = rac{S^2 Ic(S) dS}{S^2 I(S) dS}$$

where \boldsymbol{S} is the magnitude of reciprocal lattice vector and

$$S = \frac{2 \, \sin \, \theta}{\lambda}$$

where K_c is the degree of crystallinity, Ic(S) is the intensity of coherent X-ray scatter from the crystalline region, I(S) is the intensity of coherent X-ray scattered from both crystalline and amorphous regions, θ is half of the angle of deviation of the diffracted ray from the incident X-rays, and λ is the X-ray wavelength. Thermogravimetric (TG) and differential thermogravimetric (DTG) analy-

Table II¹³C-NMR Chemical Shift (ppm) ofPVA, PVA in Solution, and RPVA

Type of Carbon Atom	PVA	PVA in Solution	RPVA
)CH- CH ₂	66.68 43.85	$\begin{array}{c} 60.55 \ (+6.13) \\ 43.55 \ (+0.3) \end{array}$	66.73 43.92 38.59 35.60

ses were performed using a Perkin–Elmer thermal analyser at heating rate 20° C min⁻¹. Kinetic parameters, such as the activation energy and the frequency factor, were evaluated using the Coats and Redfern equation¹⁰ for a first-order reaction adopting a linear least square fit in Fortran 77.

RESULTS AND DISCUSSION

The DMAc-LiCl solvent system was found to be an excellent solvent system for PVA with a wide range of molecular weight. The solubility was found to be about 6.7% for PVA having viscosity average molecular weights 14,000 and 1,25,000 without any gel formation. Several issues regarding the mechanism of PVA dissolution required consideration, such as the chemical composition of PVA in solution, the uniqueness of DMAc-LiCl as the solvent system, and, also, understanding of



Figure 3 IR spectra of (a) PVA and (b) RPVA.



Figure 4 ¹H-NMR spectra of (a) PVA and (b) RPVA.

the molecular dynamics of PVA in the solvent system.

In order to ascertain the chemical composition of solution, the ¹³C-NMR spectra of 0.02/0.02/0.96 PVA–LiCl–DMAc is shown in Figure 1. The chemical shift data of the above system, along with that of DMAc and DMAc–LiCl,¹¹ are given in Table I. In Figure 1, the signals due to PVA at 60.55 (CH–) and 43.55 (–CH₂–) ppm could not be recognized at low resolution due to low concentration of PVA in the solution. From Table I, it can be seen that there was a downfield shift for all carbon atoms of DMAc upon addition of LiCl due to deshielding, having a maximum value for the carbonyl carbon atom. This is due to the direct interaction of the metal atom with the carbonyl oxygen, which decreases the electron density of the entire DMAc molecule, particularly at the carbonyl carbon, and to a lesser degree at each of other carbon atoms.¹¹ Again, on addition of PVA to the above solvent system, the chemical shift of carbonyl carbon further went downfield. This is due to further decrease in electron density on carbonyl carbon atom, which is an evidence of direct attachment of the hydroxyl oxygen atom of PVA to the carbonyl carbon atom of DMAc to form a transition state, as given in Scheme 1. Again, in comparison to ¹³C-NMR spectra of pure PVA [Fig. 2(a)], the two peaks of PVA in DMAc–LiCl at 60.55 (CH—) and 43.55 (—CH₂—) ppm showed



Figure 5 XRD pattern of (a) PVA and (b) RPVA.

Samples	X-ray Powder Diffraction Data (d' Spacing in A°)	2 heta	Crystallinity (%)
PVA	$5.441(67)^{\mathrm{a}}$	16.30	38
PVA	4.566 (100)	19.45	
PVA	3.988 (63)	22.30	
PVA	2.239(27)	40.30	
RPVA	9.776 (100)	9.05	10
RPVA	4.409 (79)	20.15	

Table IIIX-ray Diffraction Data andCrystallinity of PVA and RPVA

^a Figures in the parantheses indicate relative intensities.

upfield shifting (Table II), due to shielding of the two carbon atoms. The polar nature of the solvent decreased the electron density on the carbonyl carbon atom in presence of the salt, which tended the formation of a transition state with hydroxyl oxygen atom of PVA, giving a residual positive charge. This attracted the σ -electrons in the polymer chain by an inductive effect, thereby increasing the electron density near the hydroxyl group and, hence, causing shielding. This confirmed the above transition state of PVA in the said solvent system.

In order to study the structural changes after dissolution, the IR spectra of PVA and RPVA were taken (Fig. 3) and found to be identical, indicating no addition of new groups to the PVA chain. In the ¹H-NMR spectra of both PVA and RPVA (Fig. 4), the signals observed at 4.67, 2.08, and 1.56 ppm [Fig. 4(a)] for PVA were due to -OH, CH–, and $-CH_2$ –, respectively; whereas for RPVA [Fig. 4(b)], the peaks obtained were at 4.67 (-OH), 2.9 (CH–), 2.0 ($-CH_2$ –) and 1.56 ppm ($-CH_2$ –). As four signals were obtained, there may be four different sets of protons in RPVA.

¹³C-NMR spectra of PVA [Fig. 2(a)] showed the peaks at 66.68 and 43.55 ppm, which were due to CH— and $-CH_2$ — carbon, respectively. But for RPVA [Fig. 2(b)], besides these two peaks, two extra peaks were observed at 38.59 and 35.66 ppm (Table II). From this study, it was evidenced that a new group having a different environment in the polymer chain had been formed. The XRD patterns for PVA and RPVA were given in Figure 5, and the data obtained were tabulated in Table III. From the data, it was evident that the percentage of crystallinity of PVA (38%) [Fig. 5(a)] was reduced to 10% in RPVA [Figure 5(b)]. The increase in amorphous character in RPVA indicated that on dissolution, PVA had undergone an isomeric change; in other words, PVA, which was isotactic after dissolution in the DMAc–LiCl solvent system, had changed to atactic. Therefore, it may be suggested that the structural arrangement of PVA, as given in Scheme 2, may take place during dissolution.

The above structural change was further confirmed by thermal analysis. The TG and DTG curves for PVA and RPVA are shown in Figure 6, and thermal analyses data with kinetic parameters are given in Table IV. The thermal degradation was a three-step process. An initial small loss in weight was due to evaporation of water, followed by a rather sharp break indicating the onset of a decomposition process involving a rapid loss in weight. This break ended by a slight curvature that might be due to the formation and evaporation of some volatile products.^{12,13} It can be seen that (Fig. 6; Table IV) for both PVA and RPVA, the main thermal degradation started at 270°C and terminated at 510°C; and within this temperature range, the weight loss was found to be 66.6% for PVA, whereas it was 49.2% for RPVA. For PVA, the TG curve showed only one sharp break within the main decomposition temperature range; whereas for RPVA, there were two breaks, with the first one within the range of 270-330°C and the second within the range of 430–510°C. Again, the DTG curve for PVA gave a broad peak between 380 to 460°C; whereas for RPVA, this peak splitted into two sharp peaks at 320 and 450°C. Activation energy and the frequency factor for PVA was found to be 30.692 KJ/mol and 0.38 S^{-1} , respectively; whereas for RPVA, these data were found to be 39.948 KJ/mol and 5.3 S^{-1} in second stage and 22.543 KJ/mol and 0.082 S^{-1} for third stage. In the second stage, the frequency factor of RPVA was found to be





Figure 6 TG and DTG curves of (a) PVA and (b) RPVA.

more, which may be due to the change in crystallinity. As the activation energy for second step of RPVA is more in comparison to that of PVA, RPVA will be thermally more stable that PVA.

The intrinsic viscosity and viscosity average molecular weight of PVA and RPVA did not show any significant difference (Table V). This confirmed that there was no degradation or crosslinking of the polymer chain during dissolution in the DMAc-LiCl solvent system.

Poly(vinyl acetates) prepared from PVA in the DMAc–LiCl solvent system were then characterized. Intrinsic viscosity $[\eta]$, the viscosity average molecular weight $[M\eta]$, the acetyl content (%), and the average degree of substitution (DS) for both the esters [PVAc_(anh) and PVAc_(CD)] were noted in Table V. These values for both the esters were found to be more or less similar. The solvent system being aprotic, acetylation with acetyl chloride did not involve any chemical reaction with the solvent system. The esters were further characterized by IR spectroscopy, which gave identical peaks at 3500, (small peak due to —OH), 2950 (C—H str of —CH₂—), 1740 (C=O str for ester), 1400 (C—O str, small peak due to the unreacted —OH group), and 1250 cm⁻¹ (—C—O— str).

CONCLUSION

Thus, the DMAc–LiCl solvent system was found to be an efficient solvent system for dissolution of

Table IV Active Decomposition Temperature, Percentage of Weight Loss, Activation Energy (E_a) and Frequency Factor (A) of PVA and RPVA

	Weight Loss (%)			Active Decomposition Temperature		Activation Energy E_a (KJ/mol)		$Frequency \\ Factor A \\ (S^{-1})$		
Samples	Iª	II	III	Ι	II	III	II	III	II	III
PVA RPVA	14.4 (30–270) 18.9 (30–270)	65.6 (270–510) 49.2 (270–510)	7.0 (510–800) 12.9 (510–800)	$\begin{array}{c} 140 \\ 140 \end{array}$	380 320	$\begin{array}{c} 460 \\ 450 \end{array}$	$30.692 \\ 39.948$	 22.543	$0.38 \\ 5.3$	 0.082

^a Key: I, II, III, are the pre, second, and third stages, respectively; figures in parantheses indicate the temperature range in °C.

Table V	Intrinsic Viscosity $[\eta]$, Molecular	
Weight (M	I_{n}), Acetyl Content, and Degree of	
Substituti	ion (DS) of PVA, RPVA, PVAc _(anh) , a	nd
PVAc _(Cl)		

Sample	$[\eta]$	${M}_\eta$	Acetyl Content (%)	DS
PVA	67.2	1,24,985	_	_
RPVA PVAc _(anh) PVAc _(Cl)	$67.137 \\ 81.62 \\ 82.24$	1,24,776 2,37,000 2,39,500	46.795 48.23	0.94 0.96

PVA, in which PVA could be dissolved without any chemical change. Only a small change in the crystal structure was observed during dissolution without any degradation or cross-linking, but maintaining the chemically reactive groups intact. Acetylation of PVA was carried out with excellent results, thereby suggesting that the PVA dissolved in this solvent system could be derivatised with other reagents also.¹⁴

B. T. and C. N. S. are thankful to the Director, Regional Research Laboratory (CSIR), Jorhat, India, for kindly permitting publication of this article.

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