



Trade Science Inc.

# Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 4(12), 2008 [518-526]

## Towards [60]fullerene-tethered poly(vinyl alcohol)

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Received: 10<sup>th</sup> November, 2008 ; Accepted: 15<sup>th</sup> November, 2008

### ABSTRACT

Study of the tosylation of poly(vinyl alcohol) (PVA) using *p*-toluenesulfonylchloride (TsCl) and *p*-toluenesulfonic acid (TsOH) in DMF/amine, was undertaken. The degree of tosylation and the course of the reactions did not differ from one tosylating reagent to another. Moderate to quantitative degrees of tosylation were obtained under certain conditions. Surprisingly, the system TsCl/DMF/amine was found to promote a partial oxidation of PVA. Viscometric study and spectral analyses revealed a degradation of the starting material, resulting from chains scission and formation of unsaturations. The dissolving temperatures of the modified PVA in water, DMF, and DMSO varied with the degree of substitution, and in some cases, they decreased even to room temperature. The azidation of tosylated PVA occurred with a concomitant elimination. The fullerenation of azided PVA was low and yielded a modified PVA with good solubility.

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### KEYWORDS

Azidation;  
Fullerenation;  
Chemical modification;  
Poly(vinyl alcohol);  
Tosylation.

### INTRODUCTION

Of a particular interest are polymers that are conceived as devices for pharmaceutical purposes or components of medications. Polymers have been employed as drug carriers, for their drug release controlling property, their reduced toxicity, and their improved patient compliance. Modern polymeric carriers are increasingly presented in forms of nano and microparticles, which secure an increased efficiency of drug delivery, enhanced release profiles and drug delivery<sup>[1]</sup>. To mimic the good membrane forming properties of poly-L-lysine (PLL), Goosen et al. grafted alkylamines onto chitosan and poly(vinyl alcohol) (PVA) through the reaction with *N*-(bromoalkyl)phthalimide<sup>[2]</sup>.

That poly(vinyl alcohol) found widespread uses owes to its many distinguished properties<sup>[3]</sup>. Indeed, its

water uptake capacity makes it a useful material for hydrogel-making purposes<sup>[4,5]</sup> and pharmaceutical and biomedical applications<sup>[6]</sup>. Its biodegradability permits its consideration as a special subject of studies in view of preparing drug delivery systems; Peppas has pioneered such a wonderful area of research<sup>[4,5,7]</sup>. Crosslinked PVA hydrogel was claimed to possess a drug release capacity<sup>[8]</sup>. Moreover, PVA has been one of the most chemically transformed polymers. To cite but a few, there were reactions of PVA with fatty acid chlorides<sup>[9]</sup>, methylgallate<sup>[10]</sup>, alkylchlorophosphates<sup>[11]</sup>, diketene<sup>[12]</sup>, *n*-butyl isocyanate<sup>[13]</sup>, and reactions of glycosidation<sup>[14]</sup> and phosphorylation<sup>[15]</sup>.

Also, it has been elicited that fullerene C<sub>60</sub> and its derivatives exhibit a range of interesting biological activities such as photodynamic therapy, HIV, neuroprotection, and apoptosis<sup>[16]</sup>. Besides, these bio-

logical properties, the  $C_{60}$  derivatives were claimed to substantially improve many properties of a polymer such as photoconducting and optical properties<sup>[17]</sup>. However, fullerene  $C_{60}$  suffers from the pitfall of a limited hydro solubility, which hampers somewhat its activities. One way to realize a hydrosoluble fullerene-containing system is the complexation of fullerene with  $\beta$ -cyclodextrin via an inclusion mechanism<sup>[18]</sup>. Also, and in the aim of circumventing the near insolubility of fullerene  $C_{60}$ , it was incorporated in polymer matrices in several ways: main-chain polymers, side-chain polymers, star-shaped polymers, dendritic fullerenes, and fullerene en-capped polymers. Various forms of fullerenated-polymers were satisfactorily surveyed in the review paper of Wang et al<sup>[19]</sup>.

Our work, herein presented, was to fullerenate the poly(vinyl alcohol) (PVA) by mild means, that is, tosylation, azidation, and finally fullerenation. PVA matrix would impart a degree of solubility to the fullerenated system, a solubility that has been frequently sought for. The synergism of the biological activity of  $C_{60}$ <sup>[16]</sup> and the medical and pharmaceutical uses of PVA<sup>[20]</sup> is very incentive to synthesize a fullerenated PVA.

## EXPERIMENTAL

### Materials

The chemicals and solvents were purchased from Fluka, Panreac, Reidel-de Haën, Prolabo and Aldrich. Poly(vinyl alcohol) (PVA) was Rhodoviol 4/20 (Rhodia, ex-Rohn-Poulenc; Hydrolysis extent, %Hy, 98.2%; Ester value, EV, 11.13 mg KOH/g; the molecular weight,  $M_v$ , 25 000). DMF, DMSO, and chlorobenzene were used without further purification. Pyridine, THF, ethanol, methanol, and acetone were purified by distillation before use.

Infrared spectra were recorded using a Shimadzu type FTIR 8900 fitted with Hyper program; the samples were in the form of either cast films or KBr pellets, and BIO-RED IR SearchMaster program was employed for spectra analyses.

UV-Visible spectra were recorded using a single beam UV-Visible spectrophotometer Technicomp 8500, using bidistilled water as a solvent.

The viscometric measurements were performed in bidistilled water at 30°C with a Cannon Ubbelohde capillary viscometer 532 10/I, Schott-Gerate CT 1650. The average-viscosity molecular weights  $M_v$  were

estimated by the relation of Mark-Houwink-Sakurada,  $[\eta] = KM_v^a$  where  $[\eta]$  is the intrinsic viscosity,  $K$  and  $a$  are the Mark-Houwink constants; the latter ones were taken as  $4.28 \cdot 10^{-4} \text{ dL}^{-1} \text{ g}$  and 0.64, respectively, for these conditions<sup>[21]</sup>.  $[\eta]$  was deduced from the plot of  $\eta_{\text{red}} = [\eta] + K_H [\eta]^2 C$  where  $\eta_{\text{red}}$  is the reduced viscosity,  $K_H$  is the Huggins constant,  $C$  is the concentration of the polymer solution in  $\text{g dL}^{-1}$ .

The ester value in mg KOH/g, EV, and the hydrolysis extent, %Hy, of PVA and the modified PVAs were estimated as reported earlier<sup>[22]</sup>.

### Tosylation of poly(vinyl alcohol) with *p*-toluene sulfonylchloride (TsCl) in the presence of triethylamine (TEA), TsPVA

Into a 250 mL round-bottomed flask fitted with a condenser and a magnetic bar, were charged 1 g (0.0227 mole) of PVA and 24 mL of DMF. The system was then heated at 135°C under stirring until a complete dissolution of the polymer. The solution was then cooled down to room temperature and 11.4 mL (0,0819 mole) of TEA and 7.8 mL of DMF were added. The mixture was then stirred for 2 h before a dropwise addition of the solution of TsCl in DMF was made, and the temperature was maintained at a range of 15-20°C. Upon adding the first drops of this solution, the clear mixture thickened and turned out to yellow, then orange, and finally brick red. The temperature rose to 30°C and lasted for about 10 min before it dropped down to room temperature. The polymeric products were then isolated by precipitating the mixture in acetone. The filtered products were intensively washed with distilled water followed by acetone (until the  $\text{AgNO}_3$  test of the filtrate is negative, indicating the absence of TsCl). Purification by sequential dissolution/precipitation cycles was performed. The products were then filtered and finally dried *in vacuo* at 40°C until constant weights.

The experiments with pyridine instead of TEA were performed under identical conditions. However, an instantaneous red color was noticed upon addition of TsCl solution, and the temperature rose beyond 30°C and lasted for almost 10 min.

The experiments with *p*-toluenesulfonic acid (TsOH), as tosylating agent, followed the same protocol as with TsCl/TEA. In this case, neither a temperature rise nor a color change was noticed.

Results of the different analyses of the products from

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the above experiments are gathered in TABLES 1-5. The degree of tosylation, DT, was calculated from eq. (1) as reported earlier<sup>[23,24]</sup>, providing a UV-visible calibration curve of TsOH in bidistilled water at  $\lambda = 222$  nm:

$$DT(\%) = \frac{n_{VTs}}{n_{VTs} + n_{VA}} \quad (1)$$

Where  $n_{VA}$  can be computed from eq. (2):

$$n_{VA} = \frac{m - n_{VTs} M_{VTs}}{M_{VA}} \quad (2)$$

Where  $n_{VA}$  and  $n_{VTs}$  are the number of moles of vinyl alcohol (VA) and vinyltosylate (VTs) units, respectively;  $M_{VA}$  and  $M_{Ts}$  are the molar masses of VA and VTs, respectively;  $m$  is the weight of the tosylated PVA (TsPVA) in the solution used for UV-visible analysis.

### Azidation of tosylated poly(vinyl alcohol), AzPVA

Into a 250 mL round-bottomed flask fitted with a condenser and a magnetic bar, were charged 0.68 g of TsPVA (DT, 67.07%; EV, 70.12) and 80 mL of distilled water. The mixture was heated at the temperature of dissolution of the TsPVA, 80°C, for one hour under stirring. Once the mixture became homogeneous, it was cooled down to 20°C in order to add dropwise an aqueous solution of sodium azide (0.475 g, i.e. 7.15 mmoles, in 5 mL of distilled water). The system was allowed to react for 72 h at 20°C. The product was isolated by precipitation into acetone, filtered and washed with a plenty of methanol and acetone. The product was then dried *in vacuo* at 40°C to a constant weight (2 days).

The experiment was remade in DMF under the following conditions: temperature of dissolution, 95°C; temperature of reaction, 90°C; reaction time, 24 h. The product was isolated following the same procedure as above.

### Fullereneation of azided poly(vinyl alcohol), C<sub>60</sub>PVA

Into a 100 mL round-bottomed flask fitted with a condenser and a magnetic bar, were charged 0.04 g of AzPVA and 20 mL of DMF. The mixture was then heated until complete dissolution of the polymer. The system was cooled down to room temperature, and was then flushed with a stream of argon for 5-10 min. Under argon atmosphere, a solution of 0.02 g of fullerene C<sub>60</sub> in 2 mL of chlorobenzene was added, and the mixture was then heated at 130°C for 30 h under an

intensive stirring. The reaction mixture was brown and a minute amount of black precipitate was noticed at the bottom of the flask. After 30 h of reaction, the system was cooled down to room temperature, and the latter precipitate was filtered off. After concentrating the filtrate, 50 mL of THF was added in order to precipitate the non reacted fullerene. After a filtration, the product was isolated by precipitation into chloroform. A sticky brown paste was obtained, which was dried *in vacuo* at 40°C to a constant weight (2 days).

The degree of fullereneation was estimated by the same equations as Equations 1 and 2, substituting the subscript VTs by VNF<sub>60</sub> (vinyl aminofullerene C<sub>60</sub>), and providing a UV-visible calibration curve of fullerene C<sub>60</sub> in chlorobenzene at  $\lambda = 330$  nm.

## RESULTS AND DISCUSSION

### Tosylation of poly(vinyl alcohol), TsPVA

As far as we know and from a survey of the literature, a copolymer of vinyl alcohol (VA) and vinyl tosylate (VTs) has not been reported yet. The hydrolysis of poly(vinyl acetate-*co*-vinyl tosylate), one of its conceivable copolymer precursors, would entail the elimination of not only the acetyl group but also the tosyl group, leading merely to poly(vinyl alcohol). Thus, the only plausible path to make this copolymer is via a direct tosylation of PVA. Heinze successfully tosylated soluble cellulose, a polyhydroxylated polymeric material<sup>[25,27]</sup>. The tosylated cellulose products were applied as membranes in pervaporation technique<sup>[28]</sup>. A survey of literature reveals that there has been only one work dealing with tosylation of PVA<sup>[29]</sup>; the authors of this work aimed only at providing unsaturations within PVA by detosylation, which was used as cross-linking agent for poly(acrylic acid) to make super-absorbent materials.

Poly(vinyl alcohol) with a molecular weight of 25 000 was subjected to a chemical reaction with *p*-toluenesulfonylchloride (TsCl) or *p*-toluenesulfonic acid (TsOH) in DMF and in the presence of an amine, to yield tosylated poly(vinyl alcohol), TsPVA, as shown in SCHEME 1.

It is worth noting that PVA did not undergo scission-inducing degradation upon the dissolution work-up in DMF at 135°C, which was complete within one hour. Indeed, the intrinsic viscosities, before and after the

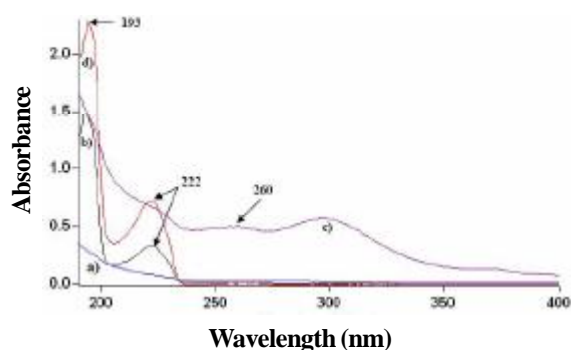
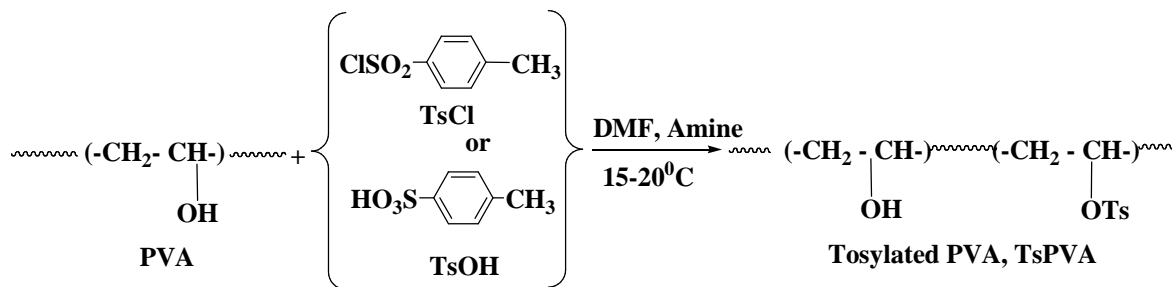


Figure 1: UV-Visible spectra in bidistilled water: (a) PVA, (b) TsPVA by TsOH, (c) TsPVA by TsCl, (d) TsOH in  $H_2O$

dissolution work-up, were measured and found to be equal to  $0.2777 \text{ dL.g}^{-1}$ . Besides, the possible degradation by a dehydration process of PVA did not occur under these conditions, as the unsaturations bands were absent in the FTIR spectrum of the treated PVA.

### Tosylation with TsCl

The reactions were first carried out in the presence of triethylamine at different  $[TsCl]/[VA]$  molar ratios and at a time of 48 h. All the soluble products produced were featured by a high film-forming ability, affording resistant and flexible orange films. In figure 1c, UV-Vis bands at 193, 222 and 262 nm are the characteristic bands of tosyl group, for  $\pi \rightarrow \pi$  and  $\pi \rightarrow \pi^*$  transitions of *p*-toluene chromophore<sup>[25,27]</sup>. FT-IR spectrum (Figure 2b) of the TsPVAs revealed two bands, 1364 and 1180  $\text{cm}^{-1}$ , attributable to the asymmetric and symmetric vibrations of the sulfonyl group,  $SO_2$ , respectively<sup>[30-32]</sup>. Unexpectedly, a conspicuous and sharp band of significant intensity in FT-IR spectrum appeared at 1716  $\text{cm}^{-1}$ ; this band existed in the virgin PVA in an insignificant intensity, but became larger upon tosylation. We assigned it to a ketone group. Thus, a concomitant oxidation

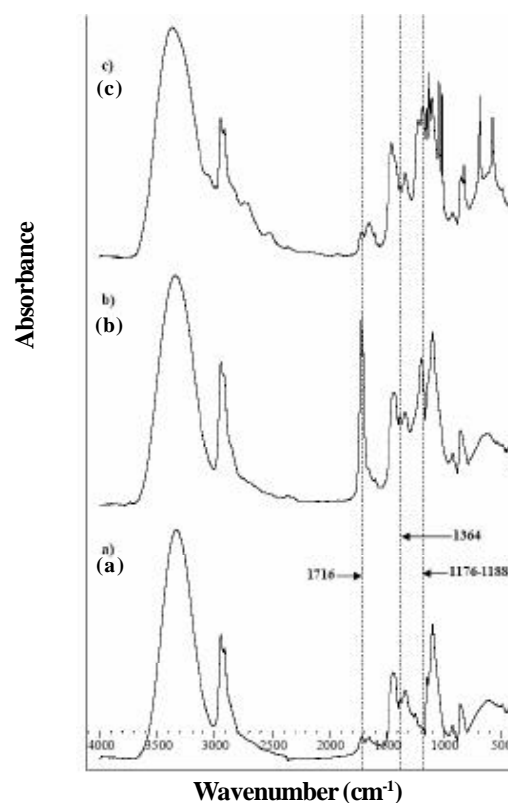


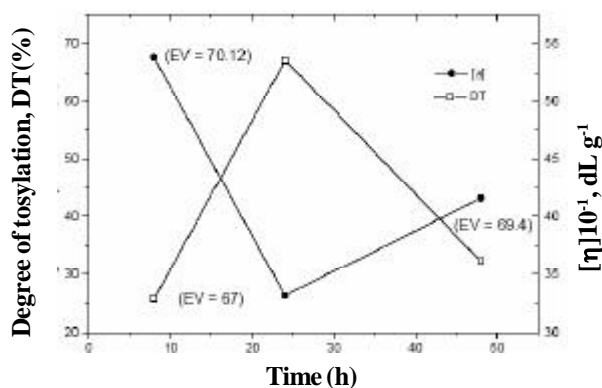
Figure 2: FT-IR spectra: (a) PVA, (b) TsPVA by TsCl, (c) TsPVA by TsOH

TABLE 1: Analyses results of the tosylated PVAs as a function of  $[TsCl]/[VA]$  molar ratio. Tosylating agent, TsCl; solvent, DMF; amine, TEA; time: 48h.

Run	$[TsCl]/[VA]^*$	EV (mg KOH/g)	$[\eta]$ ( $\text{dL}^{-1} \text{g}$ )	$M_v$ ( $\text{g.mol}^{-1}$ )	DT (%)
0	0	11.13	0.2777	25 000	0
1	1	64.51	0.3663	38 000	17.59
2	1.5	58.90	0.2652	23 000	16.09
3	2	67.32	0.5955	81 600	27.75
4	2.5	69.40	0.4160	46 600	32.25
5	3	/	/	/	/
6	4	/	/	/	/
7	5	/	/	/	/

\*  $[VA]$  = vinyl alcohol unit of PVA

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**Figure 3:** Variations of degree of tosylation, DT (%) and intrinsic viscosity,  $[\eta]10^{-1}$ , (dL<sup>-1</sup> g), as a function of time.  $[TsCl]/[VA]$ , 2.5; solvent, DMF; amine, TEA

**TABLE 2:** Dissolving temperature,  $T_{dis}$  (°C), of the tosylated PVAs. Tosylating agent, TsCl; solvent, DMF; amine, TEA; time: 48h

Run	$T_{dis}$ (H <sub>2</sub> O)	$T_{dis}$ (DMF)	$T_{dis}$ (DMSO)
0	85	135	45
1	100	swollen	RT**
2	60	115	RT
3	75	105	RT
4-a*	95	100	RT
4-b*	80	95	RT
4-c*	95	95	RT
5	insoluble	swollen	insoluble
6	insoluble	insoluble	insoluble
7	insoluble	insoluble	insoluble

\* $[TsCl]/[VA]$  = 2.5; 4-a, t = 8h; 4-b; t = 24h; 4-c, t = 48h; \*\*RT = room temperature

**TABLE 3:** Results of the tosylated PVAs as a function of  $[TsCl]/[VA]$  molar ratio and time. Tosylating agent, TsCl; solvent, DMF; amine, pyridine

$[TsCl]/[VA]$	Reaction time (h)	$[\eta]$ (dL <sup>-1</sup> g)	$M_v$ (g.mol <sup>-1</sup> )	$T_{dis}$ (H <sub>2</sub> O) (°C)	DT (%)
1	24	0,2706	23 800	55	18.22
2	24	0,2137	16 500	64	43.91
3	65	0,1615	10 600	118	77.8

might have occurred and accounted for the appearance of this band.

The remaining results are compiled in TABLE 1 and shown in figure 3. It can be noted that up to a molar ratio of 2.5, the TsPVAs obtained were soluble, and beyond this ratio, they were sparingly water-soluble and insoluble in organic solvents. Their degrees of tosylation, DT, did not exceed 32% and the trend in their intrinsic viscosities is not in parallel with that of their DTs. The intrinsic viscosity of the product of run (2) was slightly lower than that of the pristine PVA, probably due to a degradation via a detosylation of the

tosylated PVA, giving rise to unsaturations formation. This degradation would have substantially occurred for the product of the run (4). The band in the UV-Visible spectrum (Figure 1c) at about 300 nm could be attributed to a set of generated trienes. That intrinsic viscosity did not vary systematically with DT owes to the possible concomitant detosylation by a nucleophilic substitution mechanism. However, their ester values, EV, and their DTs varied likewise. From Figure 3, the reaction time of 24 h favored an appreciable substitution (67%) at the expense of a molecular weight lowering.

Generally, the tosylation of PVA enhanced its dissolving temperature in DMF and markedly in DMSO, as given in TABLE 2. In fact, most of the tosylated products were readily soluble in DMSO at room temperature. However, no appreciable improvement of the dissolution temperature in water was noticed upon tosylation.

The TsPVAs produced using pyridine instead of TEA were honey-colored. The same pattern bands of UV-Visible and FT-IR spectra were identical to those obtained using TEA. The occurrence of the plausible oxidation mentioned above was confirmed by the sharpness and intensity of the band at 1716 cm<sup>-1</sup>. It is worth mentioning that the TsCl/Py/DMF system has been widely employed as an effective condensing agent in some polycondensations such as polyesterification, where DMF acted as a catalyst<sup>[33,34]</sup>.

TABLE 3 compiles results of the tosylation in the presence of pyridine, as a function of time and  $[TsCl]/[VA]$  ratio. It can be seen that a DT as high as 78% was reached but after 65 h for a  $[TsCl]/[VA]$  of 3. However, the intrinsic viscosity was found to decrease drastically, particularly for the latter molar ratio and time. The rationale for this phenomenon would be the degradation discussed above; a severe degradation (~50%) would have taken place. The dissolving temperature of the modified PVA, obtained for these conditions, was unexpectedly high, whereas for molar ratios of 1 and 2 and the reaction time of 24 h, this temperature was interestingly lower.

The experiments in the presence of TEA or pyridine were replicated under argon atmosphere, to unveil the cause of the oxidation of PVA: was the oxygen of the air or the TsCl/DMF/TEA system responsible for the oxidation? The results were however identical to those under aerobic conditions, implying that oxygen of the

air was precluded as being the oxidizing source. Thus, it is clear that the oxidation was due to the TsCl/DMF/TEA system.

For a kinetic study of the oxidation, the product during the reaction course ( $[TsCl]/[VA] = 2.5$ ) was analyzed by UV-visible and FT-IR for every half hour for a three-hour period of time. The IR analysis results showed that the optimal oxidation was achieved at the first half hour of the reaction (the absorption of the band at  $1716\text{ cm}^{-1}$  remained unchanged beyond this time), but the tosylation increased with time. From this study, it seemed that the concomitant oxidation took place more rapidly than the tosylation. The degree of tosylation within the first 3 h did not exceed 15%.

In the tosylation of cellulose by Heinze et al.<sup>[26]</sup> with TsCl/DMAc/TEA/LiCl, the reaction was not accompanied with an oxidation. Thus, we have thought of adding LiCl to our system, hoping for an oxidation inhibition. In fact, the oxidation of PVA in the presence of lithium chloride was prevented but the tosylation extent was reduced.

As to the mechanism of the oxidation occurrence, the authors are still working out to elucidate it; yet, a

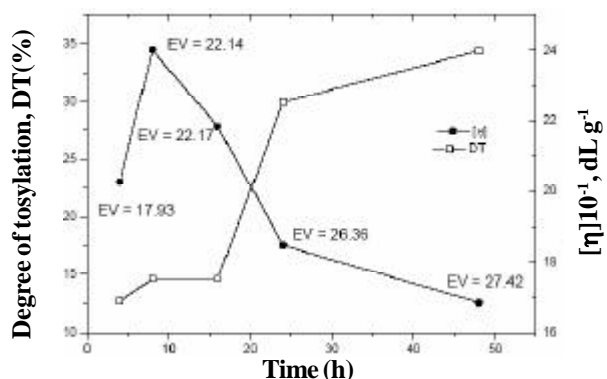
plausible mechanism may be similar to that of Swern oxidation.

### Tosylation with TsOH

Tosylation of molecular hydroxyl-containing molecules with *p*-toluenesulfonic acid (TsOH) can be achieved only in the presence of catalysts such as  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ <sup>[30]</sup>, Silica chloride<sup>[31]</sup>,  $\text{ZrCl}_4$ <sup>[32]</sup>,  $\text{Fe}^{3+}$ -montmorillonite<sup>[35]</sup>. Also, other necessary reagents were employed such as trialkyl orthoformates, alkylethers, esters, 2-alkoxybenzothiazolium salt, aryl sulfonyl methylimidazolium salts, 1-phenylsulfonyl benzotriazole, and 1-(benzenesulfonyl)- and 1-(*p*-toluenesulfonyl)-3-methylimidazolium triflates<sup>[36]</sup>.

The tosylation system TsOH/DMF/TEA was attempted for PVA, where *p*-toluenesulfonic acid (TsOH) was the tosylating agent. In the absence of a catalyst, the tosylation reaction was surprisingly successful, as confirmed by UV and IR analyses (Figures 1 and 2); the results are gathered in TABLES 4 and 5 and shown in figure 4. The TsPVAs were in form of transparent gels. The UV-Visible spectrum (Figure 1) revealed bands at 193 and 222 nm, respectively for  $\pi \rightarrow \pi$  and  $\pi \rightarrow \pi^*$  transitions of *p*-toluene chromophore of the tosyl group. FT-IR spectrum (Figure 2) showed the characteristic bands of the tosyl groups at  $1364$  and  $1180\text{ cm}^{-1}$ . Interesting was that no oxidation with this system occurred as the intensity of IR band at  $1716\text{ cm}^{-1}$  remained unchanged.

Although the tosylated PVAs were all soluble even for higher  $[TsOH]/[VA]$  molar ratios, the degrees of tosylation were not substantial; the greatest DT was about 35% (TABLE 4). It can be noticed that the higher the substitution, the lower the intrinsic viscosity (the molecular weight). Again, the reason for the intrinsic viscosity lowering could be the degradation by detosylation. As shown in figure 4, the DTs were in tune with the EVs and increased with time, but they did not attain higher values as found in the case of TsCl. The intrinsic viscosity generally declined with time. Also, this system of tosylation seemed to favor the dissolving temperatures in solvents tested. In fact, the dissolving temperatures (TABLE 5) in water were in the range of  $45$  and  $75^\circ\text{C}$  values lower than  $85^\circ\text{C}$ , that of the unmodified PVA. And, as with TsCl, the dissolving temperatures in DMSO decreased to room temperature.



**Figure 4:** Variations of degree of tosylation, DT (%), and  $[\eta]$  ( $\text{dL}^{-1}\text{ g}$ ), as a function of time.  $[TsOH]/[VA]$ , 4; solvent, DMF; amine, TEA

**TABLE 4:** Results of the tosylated PVAs as a function of  $[TsOH]/[VA]$  molar ratio. Tosylating agent, TsOH; solvent, DMF; amine, TEA; time: 48h.

Run	$[TsOH]/[VA]$	EV (mg KOH/g)	$[\eta]$ ( $\text{dL}^{-1}\text{ g}$ )	$M_v$ ( $\text{g}\cdot\text{mol}^{-1}$ )	DT (%)
0	0	11.13	0,2777	25 000	0
8	1	12.13	0,2234	17 600	13.94
9	2	16.87	0,2125	16 300	14.37
10	3	21.09	0,2071	15 700	30.13
11	4	27.42	0,1683	11 300	34.40
12	5	20.65	0,1763	12 200	27.25

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### Azidation of tosylated poly(vinyl alcohol), AzPVA

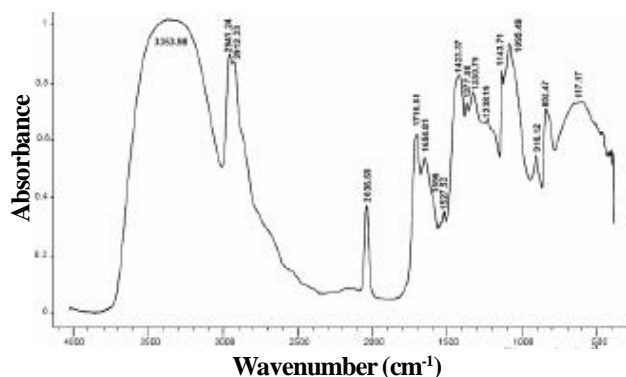
Azidation of starch, a naturally polyhydroxylated polymer, was lately studied<sup>[37]</sup> and found to be a suitable way for cross-linking the starch upon heating, to end up with interesting uses such as absorbent, paste thickener and flocculent. Azidation of poly(vinyl alcohol) was performed through the reaction of tosylated PVA with sodium azide as shown in SCHEME 2, involving a classical nucleophilic substitution.

The reaction of TsPVA (TsOH; DT, 34.40%; EV, 27.42) in water at 20°C and a time of 72 h gave a quantitative azidation as confirmed by a FTIR spectral characterization; the tosylate band at 1188 cm<sup>-1</sup> disappeared completely and a new band clearly appeared at

**TABLE 5: Dissolving temperature, T<sub>dis</sub> (°C), of the tosylated PVAs. Tosylating agent, TsOH; solvent, DMF; amine, TEA; time: 48h.**

Run	T <sub>dis</sub> (H <sub>2</sub> O)	T <sub>dis</sub> (DMSO)
0	85	45
8	45	40
9	55	RT**
10	60	RT
11-a*	55	RT
11-b*	55	RT
11-c*	60	RT
11-d*	60	RT
11-e*	65	RT
12	75	RT

\*[TsOH] / [VA]= 4: 11-a, t = 4h; 11-b; t = 8h; 11-c, t = 16h ; 11-d, t = 24 ; 11-e, t = 48. \*\*RT = room temperature



**Figure 5: FT-IR spectrum of AzPVA; solvent, water; reaction time, 24 h**

2038 cm<sup>-1</sup> which was assigned to the azide group (N<sub>3</sub>). The intrinsic viscosities [η] in DMSO of the product AzPVA and the pristine PVA were 0.6882 and 0.507 dL.g<sup>-1</sup>, respectively.

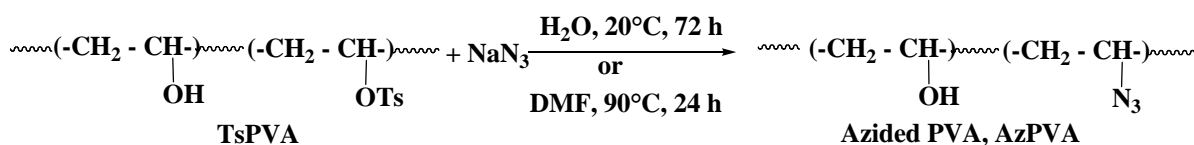
However, the on-water reaction of TsPVA (TsCl; DT, 67.07 %; EV, 70.12), a tosylated PVA with ketone groups, was carried out for 24 and 72 h, respectively. The displacement of the tosyl group by azide ion was relatively low for 24 h but substantial for 72 h (Figure 5). As can be seen in this figure, the nucleophilic substitution seemed to occur with a concomitant elimination reaction, leading to the formation of unsaturations as suggested by the two bands present at 1596.95 and 1654.81 cm<sup>-1</sup> (conjugated and non-conjugated double bonds, respectively), particularly for 72 h. The elimination process did not extensively take place in the case of TsPVA, a tosylated PVA exempt of ketone groups. The intrinsic viscosities [η] of the products AzPVA in DMSO were found to be 0.5371 and 0.89 dL.g<sup>-1</sup>, for 24 and 72 h, respectively.

The azidation in DMF proceeded at 90°C for 24 h. The modification was significant for TsPVA (TsOH; DT, 34.40%; EV, 27.42) and less substantial for TsPVA (TsCl; DT, 67.07 %; EV, 70.12). In both cases, the elimination reaction did occur, but more importantly for the latter case. The intrinsic viscosities [η] of the respective products AzPVA in DMSO were 0.4982 and 0.89 dL.g<sup>-1</sup>, values higher than that of PVA.

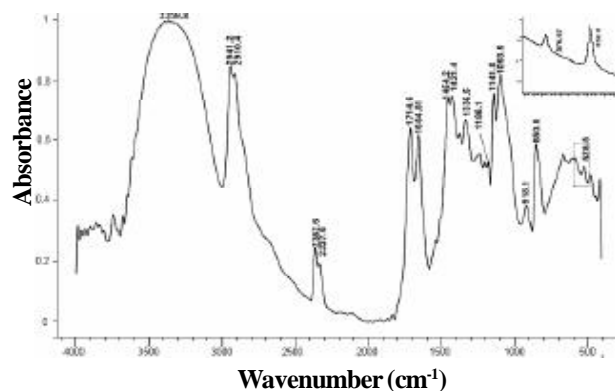
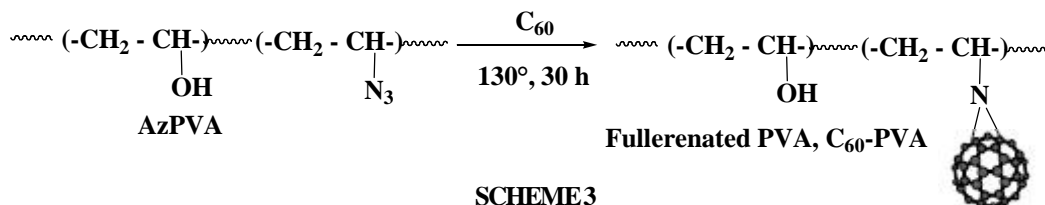
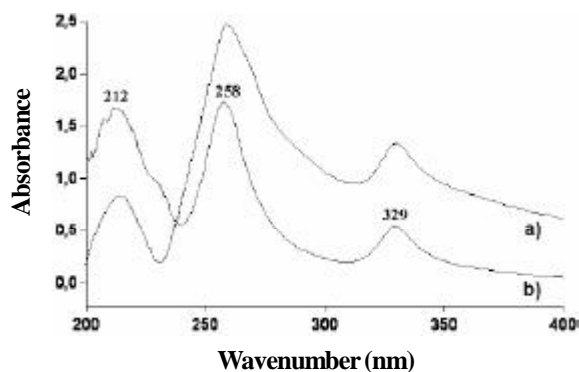
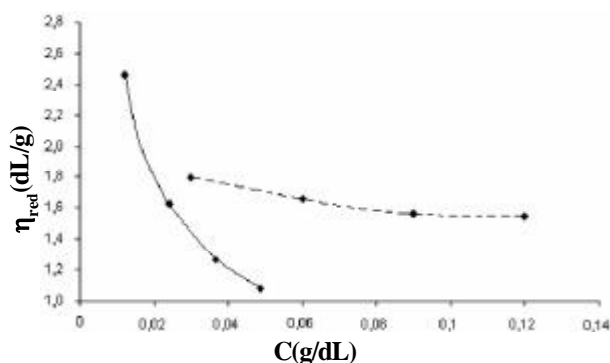
### Fullereneation of azided PVA, C<sub>60</sub>PVA

After a series of solubility tests, a 1:10 (V:V) DMF/chlorobenzene system proved to be the appropriate medium for the fullereneation of the AzPVA (the one obtained in water for 72 h), SCHEME 3. The fullereneated PVA was a brown sticky material.

A higher temperature coupled with a longer time led to a quantitative elimination of azide groups as the band at 2038 cm<sup>-1</sup> completely disappeared from the FTIR spectrum (Figure 6). The degree of fullereneation was estimated using a calibration curve for fullerene C<sub>60</sub> at λ<sub>max</sub> = 330 nm in chlorobenzene and was found,



SCHEME 2

Figure 6: FT-IR spectrum of C<sub>60</sub>PVAFigure 7: UV-Visible spectra : (a) C<sub>60</sub>PVA in THF, (b) Fullerene C<sub>60</sub> in chlorobenzeneFigure 8: Plot of the reduced viscosity vs the concentration in g dL<sup>-1</sup> of the C<sub>60</sub>PVA, η<sub>red</sub> = f(C): — DMSO ; ..... THF

however, not to exceed 2%. It is enlightening to indicate that Martinez et al. recently anchored fullerene C<sub>60</sub> on

PVC samples of different degrees of isotacticity via a homolytic pathway, taking advantage of the well-known C-Cl labile bonds, and the optimal degree of fullerene was only 7.4% in weight<sup>[38]</sup>. FTIR spectrum of the fullerened PVA (Figure 6) revealed the characteristic bands of the fullerene: 1421.4, 1186.2, 576, and 526.5 cm<sup>-1</sup><sup>[39]</sup>. Two new bands appeared at 2337 and 2362 cm<sup>-1</sup> which can be attributed to *ortho*-bonding of the benzene moiety of the fullerene with the nitrogen atom of the amino group; these two bands are usually observed for chelated benzene-containing molecules<sup>[40]</sup>. Interesting was the increased intensity of the band at 1654.81 cm<sup>-1</sup>, which would hint at an additional elimination under the conditions of fullerene, probably as a result of heating. The low degree of fullerene obtained would give an insight into the prevalence of elimination process over fullerene. Its UV-Visible spectrum in THF (Figure 7) showed characteristic bands of C<sub>60</sub> at 212, 257, and 330 nm<sup>[41]</sup>; other workers observed a band at 228 nm instead of 212 nm in our case. The absence of bands around 430 nm would suggest that C<sub>60</sub> is totally monoattached, a mono-adduct. A striking finding was that the curves of the experimental η<sub>red</sub> = f(C) of the C<sub>60</sub>PVA in DMSO and THF were found as shown in figure 8, suggesting a polyelectrolyte behavior of the polymer; the reduced viscosity decreased with increasing concentration of C<sub>60</sub>PVA. This behavior may be the result of aggregation of fullerene groups.

The C<sub>60</sub>PVA was soluble in water, DMSO and THF, a result that showed a dramatic effect of the attachment on PVA on the solubility of highly hydrophobic C<sub>60</sub>.

## CONCLUSION

The preparation of the copolymer of vinyl alcohol (VA) and vinyl tosylate (VTs) was possible via the tosylation of poly(vinyl alcohol). The effect of tosylation on the properties of PVA was evident; a solubility change of the polymer was noticed. While the reactiv-



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ity of *p*-toluenesulfonic acid (TsOH) almost equals that of *p*-toluenesulfonylchloride (TsCl) as far as the extent of substitution is concerned, it seems to be the tosylating agent of choice for hindering the occurrence of oxidation of PVA. The addition of LiCl to the reaction mixture may reduce the oxidation phenomenon. Azidation of tosylated occurs with a parallel elimination. The fullerenation of azided PVA affords a modified PVA with low C<sub>60</sub> content but with good solubility.

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