



Viscometric Study of *Bis*(cinnamaldehyde) and Their Schiff Base Polymers in DMF and THF Solution at 30 °C

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Viscometric parameter is a simplest method to determine molecular shape, size and weight. *Bis*(cinnamaldehyde) and their Schiff base polymeric solutions were prepared in DMF and THF at 30 °C, to investigate viscometric study by dilute solution viscometry method. The intrinsic viscosity and viscometric constants of these solutions were calculated by six different equations such as Huggins, Kramer, Martin and Schulz-Blaschke equations by graphic extrapolation and Solomon-Ciuta, Deb-Chatterjee equations through a single point determination, which represents the advantage of being a faster method. The thermodynamic parameters *e.g.*, ΔG , ΔS and ΔH , were also calculated by equation related with dilute solution viscometry method. The molecular mass of polymers was determined by applying Mark-Howink-Sakurada equation. The results obtained that the single point determination can be applied and Deb-Chatterjee equation showed to be the most appropriate for those calculations.

Key Words: Schiff base polymer, Dilute solution viscometry, Molecular weight, Thermodynamic parameters.

INTRODUCTION

4,4'-Methylenebis(cinnamaldehyde) (MBC) is formed from the parental compound cinnamaldehyde, having conjugated double bonds with aldehydic groups and successfully formed the Schiff base polymers with diamino compounds (such as ethylenediamine, 1,2-propylenediamine, 1,3-propylenediamine, semicarbazide and thiosemicarbazide). Previously, the dialdehyde and some Schiff base polymers had been synthesized by polycondensation reaction and also characterized¹. Characterization of this polymer has been done extensively by techniques like infrared spectroscopy (FTIR), ultraviolet/visible spectroscopy (U/V spectroscopy) and nuclear magnetic resonance (NMR). The thermal analysis as well viscosity measurement was observed from these derived Schiff base polymers^{2,3}. The solubility of *bis*(cinnamaldehyde) and their Schiff base polymeric solutions were taken in highly polar solvents (DMF/THF) at 30 °C⁴, to investigate viscometric study by dilute solution viscometry (DSV) method.

On the other hand, only some publications state viscometric measurements, but it will be helpful to match the results obtained from other techniques. However, viscometric measurement is a physical parameter and gives primary information about structure, size, shape and molecular weight of compounds⁵⁻⁷.

The viscometric method is a simple, inexpensive and sensitive analytical technique and also attractive to other methods. Dilute solution viscosity of dialdehyde and their derived Schiff base polymers were measured at various concentrations and temperatures⁸ by Oswald's viscometer. Every measurement was made at least three times. The adjustment of capillary position along vertical direction was taken and the proper control of temperature of system was maintained with Gallenkamp thermostatic water bath. Using the precaution, the variation of replicate measurements were observed with relative standard derivation (RSD) within ± 0.5 %.

The reduced viscosity (eqn. 1) provides a measurement of the polymer capacity of increasing the solution viscosity. When this parameter is extrapolated to infinite dilution, intrinsic viscosity value is obtained, in conditions where the macromolecules can be considered as isolated. Thus, from measurements of specific viscosity, it is possible to attain the intrinsic viscosity through graphic extrapolations. The specific viscosity determines the contribution of the solute to the viscosity of the solution. The quality of the solvent used, intrinsic viscosity values and some coefficients parameters are obtained from eqn. 6.

In order to apply these relations, practical determinations using different concentrations of polymer solutions are carried out by counting the efflux time of these solutions through a

capillary^{9,10}, where the two parameters K and a are related to the "stiffness" of the chain and depend on the type of polymer, solvent and temperature^{11,12}.

Dilute solution viscometry method for the determination of interaction of polymeric system has been studied. Ivana and his coworkers¹⁸ examined the viscometric study of high *cis* polybutadiene in cyclohexane and concluded that viscometric parameters determined by graphic extrapolation as well as single point determination are more rapid and suitable for high-*cis* polybutadiene. Philip¹⁴ investigated thermodynamics parameters and intrinsic viscosity measurements of hydrophobically-substituted water-soluble polymers and suggested that the intrinsic viscosity dependent on the thermodynamics function of nonionic polymer.

In the present study, the viscometry measurement of dilute solution of polymeric solutions with different concentrations has been performed based on DSV method. The viscometric parameters (intrinsic viscosity and constants values) of polymeric solution in THF have been obtained by extrapolation and single point determination as well as viscosity- average molecular mass were studied the perceptual difference of constant values of intrinsic viscosity by both methods and the average molecular mass were also compared.

EXPERIMENTAL

Cinnamaldehyde, ethylenediamine, 1,3-propylenediamine, semicarbazide, thiosemicarbazide (E. Merck, Germany) and 1,3,5-trioxane (Fluka, Switzerland), glacial acetic acid, sulphuric acid (98 %), chloroform, *n*-hexane, tetrahydrofuran (THF) and dimethyl formamide (DMF) obtained from (Fluka, Switserland) were used. Pure nitrogen obtained from British Oxygen Company (BOC), Karachi was used. Meso-stilbenediamine was prepared as reported¹⁰ from benzaldehyde *via* hydrobenzamide, acetyl-*meso*-stilbenediamine to *meso*-stilbenediimine.

Preparation of 4,4'-methylenebis(cinnamaldehyde) (MBC) and their polymers: This dialdehyde and their different Schiff base polymers were prepared as reported methods¹¹ and then the sample solutions were prepared by the procedure of dilute solution techniques, as below:

The dialdehyde (MBC) and five different polymeric solutions were prepared by adding the appropriate solvent DMF/THF with different concentrations 0.02, 0.04, 0.06, 0.08, 0.1 and 0.12 g/100 mL (w/v) of solvent, (depending on the molecular mass), at room temperature (30 °C). For the extrapolation to infinite dilution, experimental determination was carried out by counting the eluent time of all sample solutions. By single point determination, the lowest value of dilution was chosen for calculations. At low concentration, the formation entanglement (error) of polymer among the macromolecules is minimized.

Characterization: The elemental micro-analysis was taken out by Elemental Micro-Analysis Ltd, Deven, U.K. Infrared spectra were recorded on a Nicolet Avatar 330 FT- IR (Thermo Nicolet Electron Corporation, USA) with attenuated total reflectance (ATR) accessory (Smart partner) within 4000-600 cm⁻¹.

A parameter directly related to determination of viscometry is the intrinsic viscosity. Various mathematical equations are used in literature for calculating the intrinsic viscosity $[\eta]$ of a polymeric solution, by graphic extrapolation (eqn. 1-4) and from a single point viscometry measurement of dilute solution (eqn. 5-6). These equations are as following:

$$\eta_{\text{red}} = [\eta]_h + k_h [\eta]_h^2 c \quad (1)$$

$$\ln \frac{\eta_r}{c} = [\eta]_k - k_k [\eta]_k^2 c \quad (2)$$

$$\ln \eta_{\text{red}} = \ln [\eta]_m + k_m [\eta]_m c \quad (3)$$

$$\eta_{\text{red}} = [\eta]_{\text{sb}} + k_{\text{sb}} [\eta]_{\text{sb}} \eta_{\text{sb}} \quad (4)$$

$$[\eta]_{\text{SC}} = \frac{[2(\eta_{\text{sp}} - \ln \eta_r)]^{1/2}}{c} \quad (5)$$

$$[\eta]_{\text{DB}} = \frac{(3 \ln \eta_r + 3/2 \eta_{\text{sp}}^2 - 3 \eta_{\text{sp}})}{c} \quad (6)$$

where: $\eta_r = t/t_0$ is the relative viscosity (the ratio between elute time of polymeric solution and solvent), $\eta_{\text{sp}} =$ specific viscosity ($\eta_{\text{sp}} = \eta_r - 1$), $[\eta]_h = \lim_{c \rightarrow 0} \eta_{\text{red}}$, $[\eta]_k = \lim_{c \rightarrow 0} \eta_{\text{inh}}$, $[\eta]_m = \lim_{c \rightarrow 0} \ln \eta_{\text{red}}$, $[\eta]_{\text{sb}} = \lim_{c \rightarrow 0} \eta_{\text{red}}$, $[\eta]_{\text{SC}}$ and $[\eta]_{\text{DB}}$ are the intrinsic viscosities related to all above equations. k_h , k_k , k_m and k_{sb} are Huggins, Kramer, Martin and Schulz-Blaschke coefficient, respectively. Huggins and Kramer coefficients are related to chain conformation in the analysis conditions. While for many polymeric systems, the value of k_{sb} was constantly found 0.28, which is frequently applied in single point determination in many polymeric systems.

According to Mark-Sakurada equation (eqns. 5-6), the value of intrinsic viscosity changes with the molecular mass of polymers as:

$$[\eta] = KM^a \quad (7)$$

where K and a are related to stiffness of chain conformation as well as depend on type of polymer, solvent and temperature. In average-viscosity molecular mass, the constants $k = 11.2 \times 10^3$ mL/g and $a = 0.75$ were employed.

The viscosity measurements of dialdehyde (MBC) and their Schiff polymers (PMBCen, PMBCPR, PMBCSc and PMBCTSc, (Table-1) in DMF and *meso*-PMBCSt in THF with 0.02-0.12 g/dL were noted within temperatures 30 °C by using a suspended level viscometer (Technico ASTM 445). Each time 15 mL of solution was taken and average flow time of at least three readings was taken. The flow time (eluate time) of solvent at same condition was also noted. A Gallenkamp viscometer bath was used to control the temperature.

TABLE-1(a)
VARIOUS VISCOSITIES OF METHYLENEBIS(CINNAMAL-
DEHYDE (MBC) AT DIFFERENT CONCENTRATION

Concentration	Relative viscosity	Specific viscosity	Reduced viscosity	Intrinsic viscosity
0.02	1.0063	0.0063	0.315	0.2489
0.04	1.0150	0.0150	0.375	0.3289
0.06	1.0267	0.0267	0.445	0.4089
0.10	1.0505	0.0505	0.505	0.4889
0.12	1.0678	0.0678	0.565	0.5689

TABLE-1(b)
VARIOUS VISCOSITIES OF SCHIFF BASE POLYMER
(PMBCen) AT DIFFERENT CONCENTRATION

Concentration	Relative viscosity	Specific viscosity	Reduced viscosity	Intrinsic viscosity
0.02	1.01208	0.01208	0.604	0.5841
0.04	1.02656	0.02656	0.664	0.6641
0.06	1.04344	0.04344	0.724	0.7441
0.1	1.07840	0.07840	0.784	0.8241
0.12	1.10128	0.10128	0.844	0.9041

TABLE-1(c)
VARIOUS VISCOSITIES OF SCHIFF BASE POLYMER
(PMBCPR) AT DIFFERENT CONCENTRATION

Concentration	Relative viscosity	Specific viscosity	Reduced viscosity	Intrinsic viscosity
0.02	1.01274	0.01274	0.637	0.5838
0.04	1.02788	0.02788	0.697	0.6638
0.06	1.04542	0.04542	0.757	0.7438
0.10	1.08170	0.08170	0.817	0.8238
0.12	1.10524	0.10524	0.877	0.9038

TABLE-1(d)
VARIOUS VISCOSITIES OF SCHIFF BASE POLYMER
(PMBCSc) AT DIFFERENT CONCENTRATION

Concentration	Relative viscosity	Specific viscosity	Reduced viscosity	Intrinsic viscosity
0.02	1.01274	0.01274	0.637	0.5838
0.04	1.02788	0.02788	0.697	0.6638
0.06	1.04542	0.04542	0.757	0.7438
0.10	1.08170	0.08170	0.817	0.8238
0.12	1.10524	0.10524	0.877	0.9038

TABLE-1(e)
VARIOUS VISCOSITIES OF SCHIFF BASE POLYMER
(PMBCt) AT DIFFERENT CONCENTRATION

Concentration	Relative viscosity	Specific viscosity	Reduced viscosity	Intrinsic viscosity
0.02	1.01302	0.01302	0.651	0.6432
0.04	1.02844	0.02844	0.711	0.7232
0.06	1.04626	0.04626	0.771	0.8032
0.10	1.08310	0.08310	0.831	0.8832
0.12	1.10692	0.10692	0.891	0.9632

TABLE-1(f)
VARIOUS VISCOSITIES OF SCHIFF BASE POLYMER
(PMBCTSc) AT DIFFERENT CONCENTRATION

Concentration	Relative viscosity	Specific viscosity	Reduced viscosity	Intrinsic viscosity
0.02	1.01516	0.01516	0.758	0.746
0.04	1.03272	0.03272	0.818	0.826
0.06	1.05268	0.05268	0.878	0.906
0.10	1.09380	0.09380	0.938	0.986
0.12	1.11976	0.11976	0.998	1.066

The absolute viscosity η was calculated from the following equation:

$$\eta = \rho\beta t \quad (8)$$

where " ρ " is density, " β " is calibration constant of viscometer and " t " is the flow time of the liquid.

Thermodynamics parameters: The thermodynamic parameters of the solutions were determined from temperature dependence of absolute viscosity.

The activation energy (ΔG) was calculated from the equation:

$$\Delta G = 2.303RT \log \left(\frac{\eta_{\text{abs}}}{10^{-3}} \right) \quad (9)$$

where R is gas constant and T is absolute temperature. A straight line was observed by plotting $\log \eta_{\text{abs}}$ versus $1/T$.

The values of heat of activation of flow (ΔH_v) was calculated from slope $\times R$.

The entropy of activation of viscous flow (ΔS_v) was calculated from equation:

$$\Delta G_v = \Delta H_v - T\Delta S_v \quad (10)$$

RESULTS AND DISCUSSION

The results of elemental micro-analysis of *bis* compound and their derived polymers also agreed closely to the expected values. Structural formula of polymers, were confirmed by elemental analysis and spectroscopic techniques. *Biscinnamaldehyde* and Schiff polymers were insoluble in water, methanol and ethanol, partially soluble in butanol, but soluble in acetone, chloroform, THF, DMF, DMSO and DMAc.

IR spectrum of *Biscinnamaldehyde* indicated strong bands at 1682 cm^{-1} due to $\nu(\text{C}=\text{O})$ vibrations of aldehyde. All the polymers indicate a characterized band within 1680 cm^{-1} due to $\nu(\text{C}=\text{N})$ vibrations. They were also indicated two to three bands within $1615\text{-}1500 \text{ cm}^{-1}$ due to aromatic ring and $\text{C}=\text{C}$ vibration. The polymer PMBCSc indicated strong bands at 1654 cm^{-1} due to the presence of $\nu(\text{C}=\text{O})$ groups, contributed by semicarbazide. PMBCTSc indicated a band at 1240 cm^{-1} of medium relative intensity, which could be attributed to $\nu(\text{C}=\text{S})$ vibration and support the formation of the polymer.

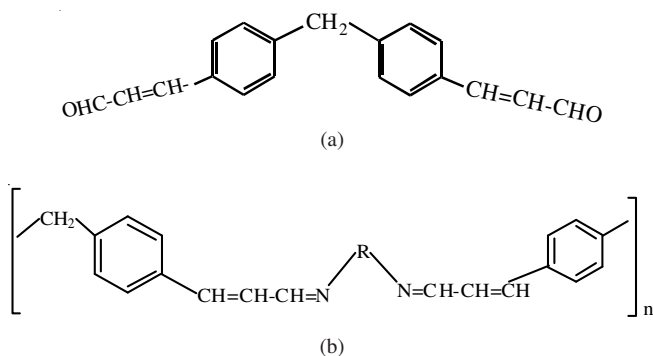
The measurements of UV/VIS spectra were carried out in THF and DMF. *Bis* cinnamaldehyde indicates two absorption bands at 262 and 338 nm with the molar absorptivity of 2.3×10^4 and $1.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ due to $\pi\text{-}\pi^*$ transition in the benzoid rings and $\pi\text{-}\pi^*$ conjugated carbonyl groups, respectively. The polymers indicated three bands due to conjugated azomethine chromophores with $\pi\text{-}\pi^*$ conjugated $\nu(\text{C}=\text{C})$ groups.

The viscosity measurements of dialdehyde MBC and newly synthesized polymers formed were recorded within 30°C with concentration within 0.02-0.12 g/dL in THF/DMF. All the primary data for all polymers were defined in detail (Table-1). Fig. 1 showed the relation between $\log \eta_{\text{sp}}$ and $\log c[\eta]$ obtained for all samples. The linear relationship indicated that all attempt were observed in Newtonian flow. For graphic extrapolation, the viscometric data were determined from eqns. 1-4. The linear relations calculated by Huggins equation for all samples. Kramer, Martin and Schulz -Blaschke equations were concerned. Intrinsic viscosity (η) is a function of molecular mass and it increased with increase in the molecular mass of polymer. The intrinsic viscosity values were obtained from all equation and their constants also calculated in (Table-2). As all intrinsic viscosity values calculated by both methods (graphic extrapolation and a single point viscometry determination) are almost equal, therefore, they were confirmed by the low percentual differences values (Table-3).

TABLE-2
VISCOMETRIC CONSTANTS CALCULATED FOR *BIS*(CINNAMALDEHYDE) AND THEIR SCHIFF BASE POLYMERS

Samples	$[n]_h^a$	$[n]_k^a$	$[n]_m^a$	$[n]_{sb}^a$	$[n]_{sb}^b$	$[n]_{s_{cb}}^c$	$[n]_{dc}^c$
MBC	2.2379	2.1579	2.2479	2.2529	2.1342	2.1291	2.1433
PMBCen	2.2674	2.1874	2.2774	2.2824	2.1492	2.1391	2.1502
PMBCPR	2.267	2.187	2.277	2.282	2.1502	2.1337	2.1512
PMBCSc	2.2673	2.1873	2.2773	2.2823	2.1511	2.1355	2.1521
PMBCSt	2.2675	2.1875	2.2775	2.2825	2.1527	2.1378	2.1537
PMBCTSc	2.2677	2.1877	2.2777	2.2827	2.1548	2.1383	2.1558

^aCalculated by graphic extrapolation. ^bCalculated through a single point determination ($k_{sb} = 0.28$). ^cCalculated through a single point determination.



R = -, PMBCen = R = CH₂.CH₂, PMBCPR = R = CH₂.CH₂.CH₂, PMBCSc = R = NHCO, PMBCTSc = R = NHCS, PMBCSt = R = CH(Ph)-CH(Ph)
Fig. 1. (a) Structure diagrams of MBC and (b) different Schiff base polymers

TABLE-3
ALL INTRINSIC VISCOSITY VALUES CALCULATED BY BOTH METHODS (GRAPHIC EXTRAPOLATION AND A SINGLE POINT VISCOMETRY DETERMINATION)

Samples	kh	kk	km	k sb	kh+kk
MBC	0.1923	-0.1693	0.1793	0.1593	-0.9720
PMBCen	0.2714	-0.2198	0.2498	0.2428	-0.1311
PMBCPR	0.2828	-0.2528	0.2758	0.2028	-0.1342
PMBCSc	0.2858	-0.2728	0.2828	0.2128	-0.3510
PMBCSt	0.2968	-0.2814	0.2898	0.2168	-0.1357
PMBCTSc	0.3268	-0.2738	0.3238	0.3031	-0.1603

The polymers were indicated higher values of intrinsic viscosities than *bis* compound. The absolute viscosity (η_{abs}) for *bis* cinnamaldehyde was observed within 0.1910-0.4352 mNS/m² as compared to polymers PMBCen, PMBCPR, PMBCSc, PMBCSt and PMBCTSc were within 0.3541-0.4001, 0.3612-0.499, 0.385-0.502, 0.4162-0.5117 and 0.4281-0.553 mNS/m², respectively. The values of ΔG_v for *bis* cinnamaldehyde were within 10.989-13.1287 KJ mol⁻¹ as compared to all polymers range from 11.28-14.815 KJ mol⁻¹. The value of ΔG_v for dialdehyde and their polymers increased with an increase in temperature as well as concentration. The values of ΔH_v increased with an increase in the concentration because more energy is required to overcome the flow of polymeric solution (Table-4). Similarly a decrease in the value of ΔH_v was observed in polymers as compared to *bis* compound, it may be because of aggregation of the molecules in polymers. The values of ΔS_v of MBC were -0.0013 to -0.0081 J/K as compared to their polymer (PMBCen) reange from -0.0112 to -0.0197 J K⁻¹. The negative sign of ΔS_v for polymers show that during flow, the molecules are becoming more extended due to the uncoiling of the polymer molecules taking place in the solution.

TABLE-4
ENTHALPY OF ACTIVATION OF VISCOUS FLOW (ΔH_v) FOR DIALDEHYDE AND DRIVED SCHIFF BASE POLYMERS AT DIFFERENT CONCENTRATIONS (KJ mol⁻¹)

Compounds	Concentration (g/dL)					
	0.02	0.04	0.06	0.08	0.1	0.12
MBC	11.69	11.621	11.505	11.445	11.38	11.311
PMBCen	8.77	8.678	8.604	8.544	8.479	8.41
PMBCPR	8.52	8.455	8.425	8.358	8.296	8.227
PMBCSc	8.099	8.089	8.0798	8.0198	7.9548	7.8858
PMBCSt	7.86	7.8501	7.8404	7.7804	7.7154	7.6464
PMBCTSc	5.67	5.549	5.469	5.409	5.344	5.275

Conclusion

In the present study, the viscosity behaviour of *bis*cinnamaldehyde and derived Schiff base polymers observed by both methods graphic extrapolation and a single point determination. According to calculations, intrinsic viscosity as well as viscosity-average mass results should be calculated by the determination of the flow time of compounds with any suitable concentration at a temperature. Schulz-Blaschke constant ($k_{sb} = 0.28$), employed to all polymeric systems in a single point determination, were also suitable for being applied in this work. As Huggin constants were lower than 0.5 indicating that DMF and THF are good solvents at 30 °C. It was also verify by negative Kramer constant which were also indicate good solvents. Deb-Chatterjee equation shows more accuracy in calculation because it is independent of any predominated constant value and gives lower percentual difference as compare to other equations.

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