

Lightscattering and Viscosities Measurements of Dilute Solutions of Some Schiff Base Polymers

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Summary: Three Schiff base polymers polymethylene-bis(salicylaldehyde)tetramethylethylenediamine (PMSATen), polymethylene-bis(salicylaldehyde)meso-stilbenediimine(meso-PMSAS) and poly-methylene-bis(2-hydroxyacetophenone)1,2-propylenediimine (PMHAPn) were prepared and indicated refractive index increments (dn/dc) within 0.223-0.241 at 436 nm and 0.155-0.130 at 546 nm. The data for dn/dc was obtained by extrapolating intercept of plot $\Delta n/c$ against concentration to zero concentration. The values of Hc/τ (τ = turbidity) were plotted against concentration and reciprocal of the intercept at zero concentration gave the molecular weight in the range of 58100-66890.

The polymers were examined for reduced, intrinsic, inherent and absolute viscosities. Thermodynamic parameters as energy of activation (ΔG_v), heat of activation (ΔH_v) and entropy of activation (ΔS_v) of viscous flow were calculated at different temperatures.

Introduction

A number of Schiff base polymers have been synthesized by condensation of dialdehydes with different diamino compounds [1-8]. They have attracted attention as catenation ligands [2, 5, 9-11], where they have been used as coordination polymers [12, 13]. The thermal stability of the Schiff base polymers is also reported as comparable to polyamides [14, 15].

The Schiff base polymers poly 5,5-methylene-bis(salicylaldehyde) tetramethylethylenediamine (PMSATen), poly 5,5-methylene-bis(salicylaldehyde) meso-stilbenediimine (meso-PMSAS) and poly methylene-bis (2-hydroxyacetophenone) 1,2-propylenediimine (PMHAPn) are easily prepared by polycondensation of 5,5-methylene-bis(salicylaldehyde) or methylene-bis(2-hydroxyacetophenone) with diamines [5, 8]. The polymers also form metal chelates [5].

The work examines the average molecular weight of the polymers by light scattering and measurements of the viscosities of their dilute solutions for the characterization of the polymers.

Results and Discussion

The polymers were prepared as reported and measurement of their IR and UV-visible spectra were in agreement with the reported values [5, 8]. The polymers PMSATen and meso-PMSAS indicated a strong band around 1630 cm^{-1} corresponding to hydrogen bonded $\nu C=N$ and two bands at $1590\text{-}80$ and 1490 cm^{-1} due to $\nu C=C$. The compound PMSATen indicated two peaks at 1380 cm^{-1} and 1370 cm^{-1} due to $C(CH_3)_2$ groups contributed from diamines. The polymers in UV region indicated two to three peaks within 241-333 nm. The measurement of refractive index increment (dn/dc) is a pre-requisite for the determination of molecular weight by light scattering and is a function of wavelength, concentration and temperature [16]. The values of dn/dc were obtained from respective plots of $\Delta n/c$ against concentration from the intercept (Figs. 1 and 2), when extrapolated to zero concentration (Table-1). The dependence of $\Delta n/c$ on concentration in PMHAPn, meso-PMSAS and PMSATen indicated a significant effect in dilute solution as compared to higher concentration. This can be attributed to the fact that solubility in the case of lower

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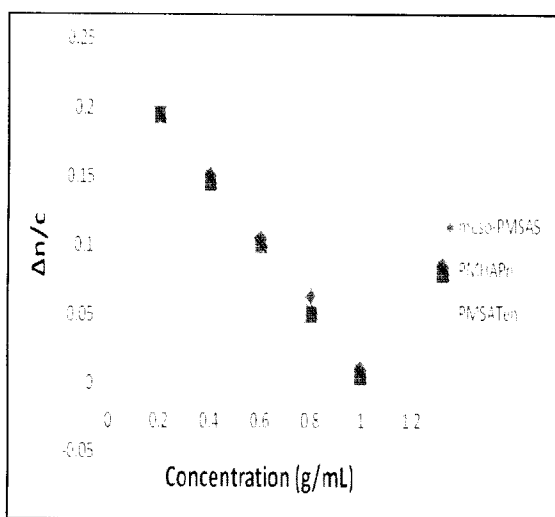


Fig. 1: Plot of $\Delta n/c$ vs conc. for meso-PMSAS, PMHAPn and PMSATen at 436 nm.

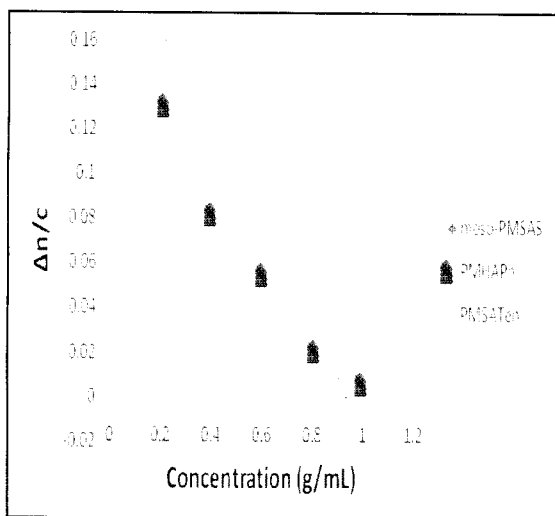


Fig. 2: Plot of $\Delta n/c$ vs conc. for meso-PMSAS, PMSATen and PMHAPn at 546 nm.

Table-1: Values of the refractive index increment (dn/dc) for Schiff base polymers in THF on room temperature.

Name of Polymers	436 nm	546 nm
PMHAPn	0.244	0.155
Meso-PMSAS	0.223	0.114
PMSATen	0.241	0.144

concentration was higher with lower enlargement as compared to higher concentration [17]. The values of $\Delta n/c$ are higher at 436 nm than 546 nm (PMHAPn = 0.195 at 436 nm and 0.123 at 546 nm).

The values of dn/dc are function of wave length and molecular weight [18]. The values decreased with increase in wave length. The value of dn/dc 0.244 for PMHAPn was observed higher than 0.241 for PMSATen and 0.223 for meso-PMSAS, may be due to slight higher molecular weight.

The values of Hc/τ for PMHAPn, meso-PMSAS and PMSATen at 436 nm and 546 nm were calculated in the range 2.97-9.98, 3.05-8.32 and 1.74-2.772, respectively (Tables-2 and 3). The values of Hc/τ were plotted against concentration (Figs. 3 and 4) and the reciprocal of the intercept at zero concentration gave the molecular weight of the macro molecules at 436 nm and 546 nm and were in the range 58105-66887 (Table-4). Molecular weight of PMHAPn 66900 was higher than PMSATen 62300 and meso-PMSAS 58100.

Table-2: $Hc/\tau \times 10^{-5}$ ($g \cdot mole^{-1}$) values for Schiff base polymers in THF at 436 nm.

Conc. g/mL	Name of Schiff base polymers		
	PHAPn	PMSATen	meso-PMSAS
0.2	2.970	1.743	3.053
0.4	5.271	2.213	4.450
0.6	7.382	2.399	5.525
0.8	9.614	2.600	7.110
1.0	9.987	2.772	8.318

Table-3: $Hc/\tau \times 10^{-5}$ ($g \cdot mole^{-1}$) values for Schiff base polymers in THF at 546 nm.

Conc. g/mL	Name of Schiff base polymers		
	PHAPn	PMSATen	meso-PMSAS
0.2	1.967	2.167	2.468
0.4	2.654	2.765	3.209
0.6	3.257	3.386	3.959
0.8	3.863	3.823	4.589
1.0	4.264	4.535	5.511

Table-4: The Molecular weight of Schiff base polymers in THF by turbidity method.

Name of polymers	Molecular weight a.m.u		
	436 nm	546 nm	Average
PMHAPn	65286	68488	66887
PMSATen	62309	62617	62327
Meso-PMSAS	57663	58548	58105

Dilute solution viscometry is commonly used for the characterization of solution properties of the polymers, estimation of chain configuration and solution power. The reduced viscosity of the polymers was calculated and the results were in the range 0.245-0.465 dl/g for meso-PMSAS, 0.453-0.618 dl/g for PMSATen and 0.34-0.96 dl/g for PMHAPn. The reduced viscosity increased with concentration and decreased with temperature. The

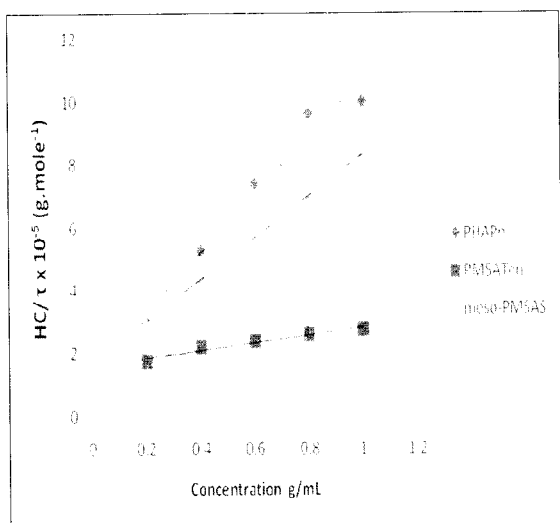


Fig. 3: $HC/\tau \times 10^{-5}$ (g.mole^{-1}) values for Schiff base polymers in THF at 436 nm.

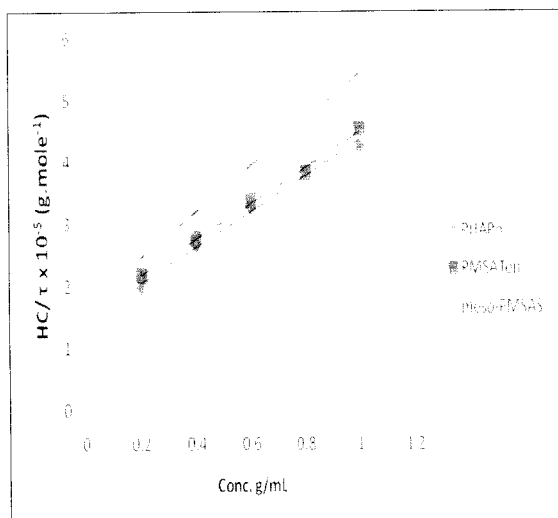


Fig. 4: $HC/\tau \times 10^{-5}$ (g.mole^{-1}) values for Schiff base polymers in THF at 546 nm.

reduced viscosity for PMHAPn was higher, corresponding to higher molecular weight than PMSATen and meso-PMSAS.

Intrinsic viscosity is a measure of volume occupied by the polymer molecule at an infinite dilution and was obtained by extrapolating reduced viscosity to zero concentration and was observed in the range of 0.208-0.499 for PMHAPn, 0.226-0.334 for meso-PMSAS and 0.436-0.463 for PMSATen within the temperature 238-323K (Table-5).

Table-5: Values of intrinsic viscosities $[\eta]$ for Schiff base polymers derived from MSA and MHA at different temperatures.

Name of Polymers	Temperature Kelvin (K)				
	283	293	303	313	323
meso-PMSAS	0.334	0.290	0.273	0.244	0.226
PMSATen	0.463	0.449	0.443	0.439	0.436
PHAPn	0.499	0.446	0.315	0.269	0.208

Temperature dependence of the viscosity was used to determine thermodynamic parameters. A linear relationship existed between natural log of absolute viscosity ($\ln \eta_{\text{abs}}$) versus $1/T$ over the concentration range studied (0.2-1.0 g/dl) (Figs. 5-7). With the help of their plots thermodynamic parameters ΔG_v , ΔH_v and ΔS_v were calculated. These parameters are sensitive to the structure formation of the polymer in the solution. ΔG_v gives information about the interaction of the polymer molecules, while ΔH_v indicates about the strength of the structure and ΔS_v shows relation about arrangement order in solution. The values of ΔG_v calculated were in the range 18.778-22.058 KJ/mole for PMHAPn, 15.042-17.062 KJ/mole for meso-PMSAS and 15.299-17.278 KJ/mole for PMSATen and the values increased with increase in the concentration and temperature.

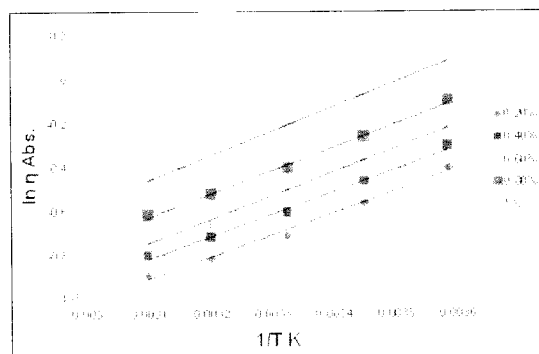


Fig. 5: Plot of $\ln \eta_{\text{abs}}$ vs reciprocal temp. for PMSATen.

The values of ΔH_v were observed in the range of 6.586-9.724 KJ/mole for PMHAPn 12.863-13.11KJ/mole for PMSAS and 10.311-11.431KJ/mole for PMSATen. Heat of activation of viscous flow are more or less independent of temperature and the results leads to suggest that polymer molecules are poorly crosslinked in THF and DMF studied. However the values of ΔH_v are increasing with concentration.

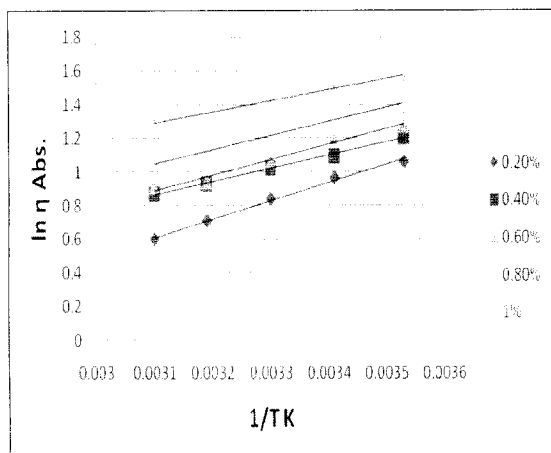


Fig. 6: Plot of $\ln \eta$ abs. vs reciprocal temp. for PMHAPn.

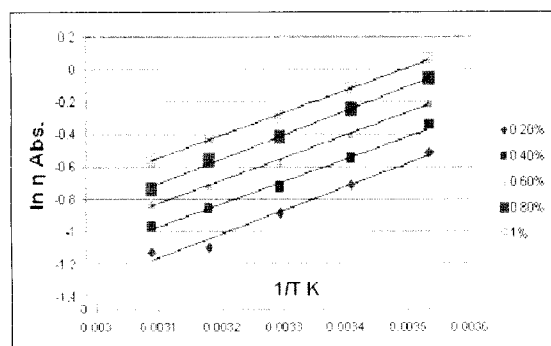


Fig. 7: Plot of $\ln \eta$ abs. vs reciprocal temp. for meso-PMSAS.

The values of ΔS_v were calculated in the range of -0.0032 to -0.048 KJ/mole for PMHAPn, -0.0076 to -0.0122 KJ/mole for meso-PMSAS and -0.0176 to -0.0481 KJ/mole for PMSATen. ΔS_v shows negative values due to system is more ordered during the flow, so the process of uncoiling and orientation of polymers takes place in the solution.

Experimental

5,5 -methylene-bis(salicylaldehyde) was prepared as reported by Marvel and Tarkey [19], methylen-bis(2-hydroxyacetophenone) was prepared as reported [8], meso-stilbenediimine was prepared from benzylaldehyde to hydrobenzamide, amarine, *N*-acetyl-*N*-benzyl-meso-stilbenediimine and meso-stilbenediimine [20]. Tetramethylenediamine (2,3-Diamino-2,3-dimethylbutane) was

prepared by the reduction of 2,3-dimethyl-2,3-dinitrobutane with granular tin in hydrochloric acid using reported method [21]. 1,2-propylenediamine was obtained from Fluka, Switzerland. The polymers PMSATen, meso-PMSAS and PMHAPn were prepared as reported [5, 8]. Potassium chloride reagent grade (E. Merk, Germany) was used as received.

Elemental micro-analysis were carried out at HEJ Research Institute of Chemistry, University of Karachi. Infra red spectra of the compounds in KBr were recorded on Perkin Elmer 1430 IR Spectrophotometer within 4000-220 cm^{-1} . Spectrophotometric studies in tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were carried out on Hitachi 220 Spectrophotometer.

The refractive index increment (dn/dc) was measured by using Brice Phoenix Differential Refractometer model No. 7109 at 436 nm and 546 nm. The refractometer was calibrated with KCl solution. The calibration constant K was calculated by plotting change in refractive index values (Δn) versus image displacement (Δd) for standard solutions of KCl. K was used to calculate Δn for PMSATen, meso-PMSAS and PMHAPn solutions at room temperature (25 °C) according to the following equation.

$$\Delta n = K \Delta d$$

The dn/dc was found by plotting $\Delta n/c$ versus C and intercept at $C = 0$ in THF. Δd of THF was noted first, followed by solution of highest concentration and Δd for other solutions in decreasing concentration order were then noted.

Universal Light Scattering Photometer model 3000-D of Brice Phoenix Co. (USA) was used. The equipment was equipped with mercury light source. Two filters for isolating mercury lines at 436 nm and 546 nm were used. A shutter with an iris diaphragm was used to control the incident beam entering the photometer and four neutral filters were used to attenuate light during measurement.

The solutions of polymers ranging from 0.2-1.0 g/ml were prepared in THF. All necessary care was taken not to allow any dust or particles to enter in the solution.

Turbidity Measurement

Turbidity measurement was made with light scattering photometer at 436 and 546 nm with square turbidity cell 30x30 mm.

The scattering ratio was obtained by measuring the intensity of the light scattered at 90° (DS), against light transmitted at 0° (DW) by the solution.

The absolute value of turbidity was calculated by using the following equation

$$\tau = [16 \text{ TD} / 3 (1.049) h] [N^2 \text{ Rw/Rc}] [aF \text{ (CD/DW)}]$$

where τ = turbidity, TD = product of diffuse transmittance of the opal reference standard and a correction value, h = width of specimen stage diaphragm, n = refractive index of the solution, Rw/Rc = correction for the residual refraction of the solvent, a = constant for opal reference standard, F = product of transmittance of reference filters required, DS/DW = scattered ratio measured of the solution.

Immersing the values of all the constants, the above equation reduces to

$$\tau = (\text{constant}) F (DS/DW).$$

The absolute turbidity was calculated from the difference in apparent turbidity of solution and solvent.

Molecular weight was determined by plotting HC/τ versus C according to the following Debye equation

$$HC/\tau = 1/H + 2Bc \text{ where}$$

$$H = 32 \pi^2 n^2 (dn/dc)^2 / 34NA$$

Which reduces to

$$H = 15.2 \times 10^{-5} n^2 (dn/dc)^2 \text{ for 436 nm}$$

$$H = 6.18 \times 10^{-5} n^2 (dn/dc)^2 \text{ for 546 nm.}$$

The intercept of the plot HC/τ versus concentration gave $1/N$, which is reciprocal of weight average molecular weight and molecular weight of the polymers PMHAPn, meso-PMSAS and PMSATen were determined.

Viscosities Measurements

Relative, specific, reduced, inherent, intrinsic and absolute viscosities with the solution of the polymers in THF at concentrations within 0.2-1.0 g/dl and temperatures 283-323K were measured as reported [22, 23].

Temperature dependence of the viscosity was used to determine the thermodynamic parameters of the polymer solution. Activation energy (ΔG_v), enthalpy (ΔH_v) and entropy (ΔS_v) of the viscous flow were also calculated as reported [24].

Calibrated Ostwald viscometer no. ATMD/445 of Technico was used for the viscosity measurement of dilute solutions in THF and DMF (0.2-1.0 g/dl). The measurement at each concentration was made at least three times. Extensive care was taken for the adjustment of the capillary position along vertical direction and proper control of system temperature was made with viscometer bath (Gallenkamp). Relative standard deviation (RSD) of replicate measurements (n=3) was observed within 0.5 %.

Conclusion

The molecular weights of three Schiff base polymers have been determined by light scattering within the range 58100 to 66890. An increase in the intrinsic viscosity also corresponded with increase in the average molecular weight of the polymers.

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