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Viscometric Study of 4,4' Naphthyl bis(oxy) bis benzaldehyde and its Schiff Base Polymers in DMAc Solution at different temperatures

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Abstract: Viscometric parameter is a simplest method to determine molecular shape, size and weight of unknown compound. In the present work, 4,4' Naphthyl bis(oxy) bis benzaldehyde and its Schiff base polymeric solutions were prepared in DMAc at different temperatures, to investigate dilute solution viscometry (DSV). These Schiff base polymers were prepared by polycondensation reaction of dicarbonyl compound 4,4' Naphthyl bis(oxy) bis benzaldehyde (NBOB) and diamines (ethylenediamine and 1,2-propylenediamine). The elemental microanalysis results are in good agreement with the theoretical values calculated. Polymeric solutions were characterized by FTIR, UV-Vis and ^{1}H-NMR spectroscopic techniques. The intrinsic viscosity and viscometric constants of these solutions were calculated by specific equations such as Huggins and Kramer. Actually the viscosity behavior of macromolecular substances in solution is one of the most frequently used approaches for characterization. It was observed that the variation of viscosity number with concentration depends on the type of molecule as well as the solvent. The thermodynamic parameters (ΔG, ΔS and ΔH) were also calculated. The accuracy and validity of these methods were evaluated.

Keywords: Schiff base polymer; Characterization, Viscometry; dilutes solution; thermodynamic parameters.

1. INTRODUCTION

4,4' Naphthyl bis(oxy) bis benzaldehyde (NBOB) is formed from its parental compound p-florobenzaldehyde and 1,4- naphthaquinone in dry dimethyl acetamide (DMAc), and successfully used for further polymerization. These polymers are the important class of polymer due to their tremendous nature. They have different behavior like thermally stability **(**Saegusa**,** *et. al.* 1992 **;**Banerjee, *et. al.* 1995**)**, chelating property **(**Banerjee, *et. al.* 1996**;** Gutch, *et. al.* 2001), high mechanical strength (Kaya, *et. al.* 2002; Yildiz**,** *et. al.* 2004), semi conducting nature (Grigoras**,** *et. al.* 2004 **;**Marin, *et. al.* 2006**)**. These Schiff base polymers contained especially ether linkage in the polymer structures (Kumar**,** *et. al.* 2008**;** Akira, *et. al.* 2008). These compounds were well dissolved in highly polar solvents **(**Aly, *et. al.* 2012). The viscometric measurements were investigated using dilute solution viscometry (DSV) have been reported **(**Jeong**,** et. al 1991**;** Avram, *et. al.*, 2011**)**. The viscometric method gives primary information about structure, size, shape and molecular weight of compounds (Kanabara**,** *et. al.* 2001**;** Kaliyappan**,** *et. al.* 2004).

The reduced viscosity is the ratio between specific viscosities and corresponding concentration of the solutions at the same temperature. The specific viscosity determines the contribution of the solute to the viscosity of the solution. Ivana (Ivana, *et.al.* 2006) conducted on the viscometric study of high cis polybutadiene in cyclohexane and revealed that viscometric parameters determined by graphic extrapolation as well as single point determination are more rapid and suitable for high-*cis* polybutadiene. An other scientist **(**Philip, *et. al.* 2012) examined different thermodynamics parameters and intrinsic viscosity measurements of hydrophobically-substituted water-soluble polymers and concluded that the intrinsic viscosity is dependent on the thermodynamics function of nonionic polymer.

The present study represents some newly synthesized dialdehyde (NBOB) and its Schiff base polymers, their characterization and viscometry measurements were measured in DMAc by DSV (dilute solution viscometry) method.

2: EXPERIMENTAL

2.1: Reagents and Chemicals:

Analytical reagent grade chemicals p-floro benzaldehyde, 1,4- naphthaquinone, ethylenediamine, 1,2-propylindiamine, dimethyl acetamide (DMAc), tetrahydrofuran, acetone , n-hexane, m-cresol, K_2CO_3,, methanol and ethanol were purchased from(E. Merck, Germany).

2.3: Preparation of 4, 4′–Methylenebis (cinnamaldehyde) (MBC) and its polymers:

The compound dialdehyde 4, 4'-[naphthyl bis (oxy)] bis benzaldehyde was prepared and purified by

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following a previously reported work **(**Banerjee, *et. al.* 1996)**.**

(i) Synthesis of dialdehyde of 4,4'-[naphthyl bis(oxy)]bis benzaldehyde:

In to a 250 mL three necked, round –bottom flask equipped with a reflux condenser, was placed (0.02M) of p-florobenzaldehyde in nitrogen atmosphere and was added (0.01M) of 1,4- naphthaquinone in dry dimethyl acetamide (DMAc) slowly and gradually in the presence of anhydrous (0.5 g) K_2CO_3. The temperature of the hot plate was maintained at 165 ^oC for 5 h with constant magnetic stirring. The reaction mixture was poured in 1000 mL of cold water and allowed to stand for 24 h. The solid product was filtered and recrystallized from the mixture of acetone and n-hexane. The crude precipitates were separated by filtration, dried in oven at 100 ^oC. The melting point was found to be > 280 ^oC.

(ii) Synthesis of Schiff base polymers from 4, 4'-[naphthyl bis (oxy)] bis benzaldehyde:

(Ethylenediamines 0.005 M (0.3 mL) and 1,2-propylenediamines (0.37 mL), was dissolved in 15 mL of m-cresol. The mixture was heated till the solution became clear. Monomer (4, 4'-[naphthyl bis (oxy)] bis benzaldehyde) was added (0.005 M, 1.72 g) at room temperature and stirred overnight. The contents were refluxed for 4 hours at 100 ^oC and the solution was poured in 100 mL of methanol. The mixture was filtered and washed with hot H_2O. The precipitates were recrystallized from DMAc and n- hexane. The melting point was found to be > 330 ^oC.

2.3: CHARACTERIZATION:

The elemental micro-analysis was carried 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 attanulated total reflectance (ATR) accessory (Smart partner) within 4000-600cm^{-1}. UV/Vis spectrophotometric studies were carried out in DMAc on a double beam Hitachi 220 spectrophotometer, (Hitachi (Pvt) Tokyo, Japan), with dual 1 cm silica cuvettes within 180–700 nm.

The nuclear magnetic resonance ^{1}H-NMR spectra were recorded at HEJ Research Institute of Chemistry, University of Karachi, on a Bruker ACF300 NMR spectrometer using dimethylformamide (DMF) as solvent and tetramethylsilane (TMS) as an internal reference at HEJ, Research Institute of Chemistry, University of Karachi. The reduced viscosity is the ratio between specific viscosity which obtained from (Eq. 1) at the same temperature.

For dilute solutions

$\eta_{rel} = t / t_o$ ……………………………….. Eq:**(1)**

where t and $t_o$are the flow time of the polymer solution and solvent respectively. Specific viscosity is the relative viscosity of the polymeric solution of known concentration over that of the solvent. It is usually determined at low concentration of the polymer. Various mathematical equations are used in literature for calculating the intrinsic viscosity [η] of a polymeric solution, by graphic extrapolation (Eq. 1 - 4). These equations are as following:

$\eta_{sp} = \eta_{rel} - 1$ …………………………….. Eq:**(2)**

$\eta_{red} = \eta_{sp} / C$ ……………………………. Eq:.**(3)**

$\eta_{inh} = \text{Ln}\ \eta_{rel} / C$ ……………………….….. E q:**(4)**

where: $\eta_r = t / to$ is the relative viscosity (the ratio between elute time of polymeric solution and solvent), η_{sp} = specific viscosity ($\eta_{sp} = \eta_r - 1$), $[\eta]_h = \lim_{C\to0} \eta_{red}$ and $[\eta]_k = \lim_{C\to0} \eta_{inh}$ are the intrinsic viscosities related to all above equations. k_h and k_k are Huggins and Kramer coefficient respectively.

Intrinsic Viscosity ([η]) is the ratio of specific viscosity of solution to the concentration of solute, extrapolated to zero concentration. Intrinsic viscosity reflects the capability of a polymer in solution to enhance the viscosity of solution and calculated by determining the reduced viscosity and extrapolating to infinite dilution using Huggins's and Kramer's equations (Eq. 5- 6) respectively.

$\eta_{red} = [\eta] + K_H [\eta]^2 C$ ……………………….Eq: **(5)**

$\eta_{inh} = [\eta] - K_K [\eta]^2 C$ ………………………Eq: **(6)**

The absolute viscosity depends on the density of polymeric solution with per unit flow time of liquid, which is calculated from Eq. (7):

$\eta = \rho\ ß\ t$ …………………………………… Eq: **(7)**

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

(a) The activation energy (Δ G) was calculated from the Eq. (8):

$\Delta G = 2.303\ RT \log (\eta ab\ s / 10^{-3})$ ……………. **Eq: (8)**

where R is gas constant and T is absolute temperature. A straight line was observed by plotting Log ŋab s verse 1/T.

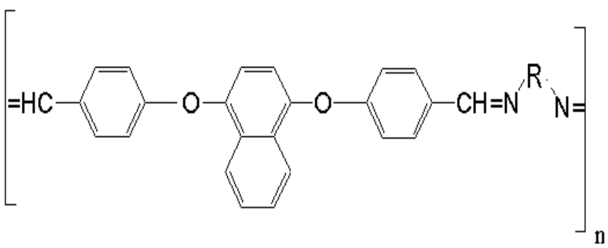
(b) The values of heat of activation of flow (ΔHv) was calculated from Slope X R.

(c) The entropy of activation of viscous flow (ΔSv) was calculated from Eq. (9):

$\Delta Gv = \Delta Hv - T\ \Delta Sv$ ……………………. **Eq: (9)**

3: <u>RESULTS AND DISCUSSION</u>

The data of elemental micro-analysis of monomer (NBOB) and their derived polymers agreed closely to the theoretical values. The structural diagram of derived Schiff base polymer is shown in **(Fig: 1).** The monomer and its Schiff base polymers were soluble in THF, DMF, DMSO and DMAc. The derived Schiff base polymers PNBOBen and PNBOBPn showed weak or medium intensity bands within 3172- 2878 cm^{-1} region due to aromatic and aliphatic C-H stretching vibrations. Both Schiff base polymers gave rise to a characteristic peak around 1616- 1644 cm^{-1} due to υC=N vibrational frequencies **(Fig: 2)**. Spectrophotometric studies were carried in THF and DMF. The first and second absorption bands appeared within 240- 265 nm due to $\pi - \pi^*$ transition in benzoid and naphthyl rings. The absorption bands in polymers as characterized band appeared within 318-345 nm, are a result of the π - π^* transition of conjugated C=N bending (azomethine group).



PMBCen, R=CH2·CH2
PMBCPh, R=*o*-C6H4

Fig 1: Structural diagram of Schiff base polymer of 4,4'-[naphthyl bis(oxy)]bis benzaldehyde.

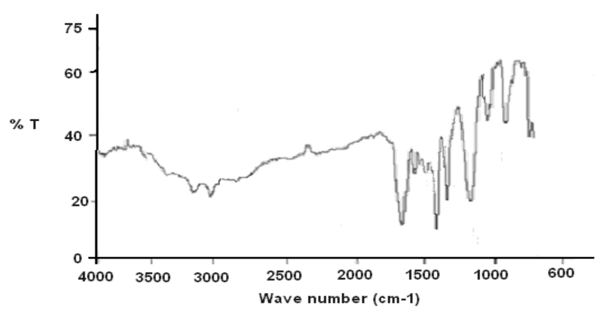


Fig 2: FT –IR spectrum of Schiff base polymer of poly {4,4'-[naphthyl bis(oxy)]bis benzaldehyde} ethylenediimine.

The structure of dialdehyde and polymers was confirmed by ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of dialdehyde showed a very clear peak of aldehyde group at δ = 8.7, while it was reduced for polymer in DMF, and both showed phenyl peaks at δ = 7.4–6.6 due to the aromatic nature of compounds **(Fig. 3).** The viscosity measurements of monomer (NBOB) and its Schiff base polymers were recorded within different concentration, 0.02-0.12 g/dL in DMAc**.** The intrinsic viscosity values were obtained from all equation**,** and their constants are given in **(Table: 1).** The Huggins's constant is independent of molecular weight of polymer. The value of K_H and PNBOBPn obtained were 0.38 and 0.45, which

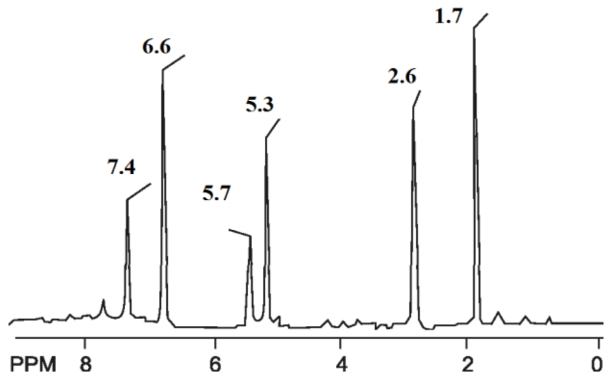


Fig. 3: ^{1}HNMR spectra of poly {4,4'-[naphthyl bis(oxy)]bis benzaldehyde} ethylenediimine. in DMF

increased in these polymers with decreasing ionic strength. The values of Huggin's constant of dialdehyde (NBOB) and its polymers were higher than 0.5, implying that DMAc is a poor solvent for these compounds. The absolute viscosity of dialdehyde (NBOB) and polymers increased with increasing the concentration with respect to their molecular weight of polymers and decreased at high temperature **(Fig. 4)**.

Table: 1: Intrinsic viscosity of 4, 4'-[naphthyl bis(oxy)] bis benzaldehyde and it's Polymers at different temperatures. (m.N.S/m^2)

Compounds	Temprature (K)				
	283	293	303	313	323
NBOB	0.348	0.324	0.299	0.286	0.273
PNBOBen	*0.482*	*0.453*	*0.439*	*0.4216*	*0.404*
PNBOBPn	0.498	0.473	0.448	0.423	0.418

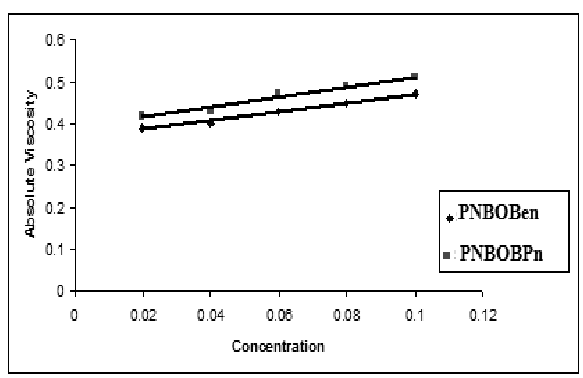


Fig: 4: Absolute Viscosity v/s Concentration for monomer (NBOB) and its Schiff base polymers (m.N.S/m^2)

4. CONCLUSION

In the present study, the viscosity behavior of 4,4'-[naphthyl bis(oxy)]bis benzaldehyde and its derived Schiff base polymers observed by dilution solution viscosity (DSV). All type of viscosity increased with increase in concentration due to the high molecular weight of macromolecules. According to calculations, intrinsic viscosity gave information about the flow time and maximum absolute viscosity of PNBOBen (0.45 **m.N.S/m^2**) and PNBOBPn (0.522 **m.N.S/m^2**) at 283 K temperature. As Huggin constants were lower than 0.5 indicating that DMAc is poor solvents for these compounds. These polymeric solutions were also used to measure the thermodynamic parameters, free energy of activation (ΔG_v), enthalpy (ΔH_v) and entropy (ΔS_v) of the system. These thermodynamic relationships gave an idea about the structure and orientation of polymeric molecules in dilute solution. The precision and validity of compounds are important tools for quality control laboratories.

REFERENCES:

Aly. K. I, (2012) "New polymer syntheses novel conducting polymers and copolymers based on 4-Teriary butyl-cyclohexanone moiety in the main chain", *J. Appl. Polym. Sci*., 123 **(6)**: 3390-3401.

Akira. M., K. Yujiro. A. J. Hiroyuki. (2011) "Characterization of resulting network polymer precursors in stepwise crosslinking diepoxide/diamine polymerization" *J. Polym. Sci. A*, 49 **(18):** 3997-4004.

Avram. I. S., G. I. Emil. I. Silvia. (2011) "Miscibility properties of quaternized polysulfone blends with polystyrene and poly(4-vinylpyridine)", *J. Polym. Compos*., **(32):** 1661-1670.

Banerjee. S., P. K. Gutch. C. Saxena. (1995) "Polyether azomethines. I. Synthesis and characterization", J. Polym Part: A, 33 **(10)**:1719-1725.

Banerjee. S., C. Saxena. P. K. Gutch. (1996) "Synthesis and characterization of polyetherketoimines" Eur Polym J. **(32)**: 661-664.

Gutch. P. K., S. Banerjee. D. C. Gupta. D. K. Jaiswal. (2001) "Poly-Schiff bases. V. Synthesis and characterization of novel soluble fluorine-containing polyether azomethines", J Polym Sci : Part A, 39 **(3)**: 383-388.

Grigoras. M., C. O. Catanescu. (2004) "Synthetic macromolecules containing π-conjugated systems compounds", J. Macromolecule Sci: Part C, 44**(2):** 131-173.

Ivana. L, M. C, Mello. M. B. Delpech. Coutinho. F.M.A (2006) "Viscometric Study of High-cis Polybutadiene in Toluene Solution", *J. Braz. Chem. Soc*., **(17):** 194-199.

Jeong. H, Y. Oishi. M. Kakimoto. (1991) "Synthesis and characterization of new soluble aromatic polyimides from 3,4-bis (4-aminophenyl)-2,5-diphenylfuran and aromatic tetracarboxylic dianhydrides", *J. Polym. Sci. Polym. Chem*., 29 **(1)**: 39-43.

Kaya. I, M. Yıldız. S. Koyuncu. (2002) "The synthesis and characterization of new oligo(polyether)s with Schiff base type", Synthetic Metals, 128 **(3):** 267-272.

Kumar. A, M. Agarwal. M. Ajai. K. Singh. (2008) "Schiff bases of 1′-hydroxy-2′-acetonaphthone: Synthesis, structures and applications in C–C coupling reaction." J. Organometal Chem, 693, 23 **(1):** 3533-3545.

Kanabara. T., Y. Kawai. K. Hasegawa. (2001) "Preparation of polythioamides from dialdehydes and diamines with sulfur by the Willgerodt–Kindler type reaction", *J. Polym. Sci. A*, 39 **(21)**: 3739-3750.

Kaliyappan. T., S. Rajagopan. P. Kannan. (2004) "Synthesis and characterization of new polymers" *J. Appl. Polym. Sci*., 91 **(1)**: 494-500.

Marin. L., V. Cozan. M. Bruma. V. C. Grigoras. (2006) "Synthesis and characterizations of new poly (azomethine- ether)" J. Eur. Polym J. 42 **(5):** 1173-1182.

Philip, M. (2012) "Thermodynamics of noncovalent interactions in hydrophobically-substituted water-soluble polymers from intrinsic viscosity measurements: Application to nucleobase-substituted pullulans", *J. Appl. Polym. Sci., 123* **(2):** 657-671

Saegusa. Y., T. Takashima. S. Nakamura (1992) "Synthesis and characterization of 1,3,4-thiadiazole-containing polyazomethines and copolyazomethines", J. Polym. Sci, Part A, 30 **(8):** 1375-1381.

Yildiz. M., (2004) "Synthesis and spectroscopic studies of some new polyether ligands of the Schiff base type", Spectroscopy Letters, 37 **(4):** 367-381.