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VISCOMETRIC STUDY OF CARBOXYMETHYLATED OLIGOIMIDES.

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ABSTRACT

Various Amino terminated oligoimides were prepared by reported method. Bismaleimide and Diaminediphenylmethane at different molar ratios were carried out. The carboxymethylation of this oligoimides was claimed out by their reaction with monochloro acetic acid. The resultant carboxymethylated oligoimides (CMOIs) were characterized. The viscosity measurement of solutions of all CMOIs was calmed out in DMF at $30^o \pm 0.3^oC$. The ubbelohde suspended type viscometer was used for such measurement. The viscosity data of the solution of CMOI signified that the decrease in concentration of solution increases reduced viscosity (η_{red}). This suggests the CMOI act as polyelectrolyte of anionic type. Thus the viscosity of the solution in DMF suppressed by adding water and KBr in DMF. Thus the viscosity measurements of solution of CMOI in DMF-Water-KBr (80:20:1%) gives the intrinsic viscosity. Also applying empirical equation is able to represent the viscometric data for all the oligoimides. It may be stated that as the equation is quite empirical.

$$\eta_{sp/c} = Z = [\eta] + \frac{k[\eta]}{C^{1/2}}$$

KEYWORDS: Polyelectrolyte, Oligoimides, Ubbelohde viscometer, reduced viscosity, empirical relation and intrinsic viscosity.

INTRODUCTION

Polyelectrolyte carried opposite (+ & -) charges on their repeating units. In solution they form a charged polyion surrounded by an atmosphere of small, mobile counter ions.[1,2] Both the repulsive and the attractive electrostatic interactions between these + ve or -ve charged species represent dominant factors influencing the behavior of polyelectrolytes in solution. The amphiphilic polyelectrolytes, exhibit solution properties arise from the competition between the hydrophobic and electrostatic interactions.[3,4] Polyelectrolyte can be effects arising from intra-chain electrostatic forces between charges presented on the chain backbone. For example, the well-known behavior of upward bending of reduced viscosity versus the concentration plot of electrolyte solution in the dilute concentration region is designated to the intra-chain electrostatic repulsion of charges on the same polymer skeleton. This also affects to chain extension and an increase of reduced viscosity upon dilution.[5,6] Besides the theoretical interest, both the electrostatic and hydrophobic interactions play an important role in biological systems as well as in technological and environmental applications, such as: paper processing, film coating, flocculants, biomedical devices and drug formulations, membranes, and so on.[7] These interactions are strongly sensitive to some parameters, like: the chain length, the charge density, the polyelectrolyte concentration, the counter ion type, the ionic strength, the solvent polarity, the length and content of hydrophobic groups, etc.[8,9]

The amino terminated oligoimides derived from Diaminediphenylmethane and Bismaleimide are reported in literature.[10] Their modification by carboxymethylation has not been reported. It such derivation of such oligoimide is carried out, the resultant oligoimide may act as polyelectrolyte. So the present communicant comprises the synthesis, characterization and viscometric study of carboxymethylated oligoimide. The work is shown in **Scheme 1**.

Experimental

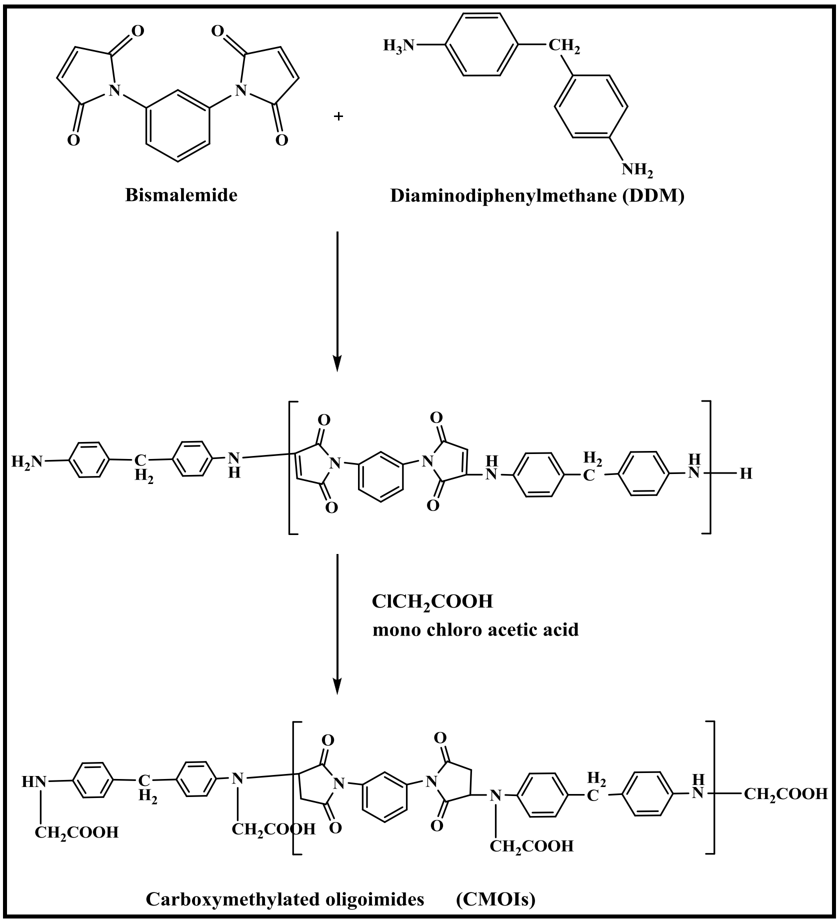
MATERIALS AND METHODS

Oligoimides were prepared by reported method.[10] All of the chemical used were of pure grade. The viscometer bath was used with maintaining temperature $30^{o} \pm 0.3^{o}C$.

Synthesis of Carboxymethyl OI

All the four oligoimides[10] were treated with monochloro acetic acid to afford carboxymethyl OI. The method was adopted as method reported for the preparation of caboxymethyl cellulose. The general procedure is as follow.

To a solution of oligoimide (Listed in **Table-1**) in acetone was added by 0.1M Sodium methoxide dissolved in methanol. The suspended pasty mass was obtained. To this resultant mass the solution of monochloro acetic acid in water added stoichiometrcally. The solid precipitates of carboxymethyl OI was obtained, filtered, washed by petroleum ether and air dried. The products were designated as CMOI- 1 to -4. Their details are furnished in **Table-2**. The detail scheme is as follow.



Scheme-1. The Synthetic route for the formation of CMOIs

Measurements

The relative, specific and reduced viscosity of the CMOI solutions from the flow times of solutions was measure by using the Ubbelohde capillary viscometer. The viscosity measurements were carried out at a constant temperature of $30^{o} \pm 0.3^{o}C$. The temperature of solution was controlled by a thermostat in a circulating bath and monitored by the thermometer. A stopwatch with a resolution of 0.1s was used to measure the flow times. By plotting the reduced viscosity (dL/g) of oligoimide solutions against concentration (g/dL), extrapolating to infinite dilution and taking the intercept, the intrinsic viscosity [ƞ] is determined.

RESULTS AND DISCUSSION

All the four oligoimides i.e. **CMOI- 1** to **4** were in form of amorphous power. The reduced viscosity of the CMOI solution in to the DMF solvent is shown in **Figure 1** as the function of oligoimide concentration. It is seen from the **Figure 1** that the reduced viscosity increases with the decreasing oligoimide concentration. This typical polyelectrolyte behavior like this for the reason that the carboxylic groups on the oligoimide chain can ionize in the polar solvent and also the effective electrostatic repulsion makes this oligoimide chain highly extended.[11,12] In this case measurement could not be performed at sufficiently low concentrations owing to the comparatively low viscosity of these solutions. The polyelectrolyte either cationic or anionic oligoimides have special viscosity behavior in association with neutral oligoimides. Neutral oligoimides have the properties that reduce viscosity increases with the increase of oligoimide concentration.

The effort was finished to determine the viscosity in mixed form of DMF and water (80:20) solvent system. The results are also parity to neat solvent. This may caused by addition of water the ionization of polyelectrolyte decreases due to the dielectric constant. The dielectric constant has a significant effect on the strength and range of electrostatic interactions.[13,14]

Figure 2: shows the reduced viscosity as a function of oligoimide concentration in the presence of DMF-water- KBr (80:20:1%). The mechanism of the KBr effect on reducing the polyelectrolyte effect mainly is related to the reduction of double layer thickness on the polyelectrolyte molecule. Due to high degree of ionization, KBr reduces the partial ionization of polyelectrolyte and eliminates the polyelectrolyte effect at lower concentration. When small molecule electrolyte is added to the polyelectrolyte solution depending on the concentration, the viscosity behavior changes.[15] It is seen from **Figure 2** that there is not electrolyte effect and viscosity does not increase with decreasing oligoimide concentration, which is in contrast with salt-free solution.

Viscosity of a given solution of oligoimides depends upon the interactions between the oligoimide chain and upon the hydrodynamic volume of the oligoimide. In the present case the solution contains a polycarboxylate ion. Because of lower shielding of the COO^- ions present in the oligoimide chains, the oligoimide chains will keep away from each other to minimize the repulsive interaction. With increase in dilution, the number of solvent molecules per molecules of oligoimide chain would increase. Hence number of solvent molecules surrounding each ion on oligoimide chain would increase. The repulsive interaction of oligoimide chain would decrease. Due to association of COO^- with larger number of solvent molecules the hydrodynamic volume would also increase. With increase in dilution the strength of repulsive interaction decreases and the hydrodynamic volume increases. As a result the viscosity functions would increase with decrease in concentration of oligoimide solutions.

In case a circumstance is produced such that, (i) The negatively charged ion is well surrounded by an equal number of both +ve and –ve ions, the polyelectrolytic behavior will not be observed. This situation is created by adding a strong electrolyte to the solvent in which the viscometry is carried out. (ii) The negatively charged ions of the poly ionic species are very well solvated even in concentrated solution to the extent that, on further dilution there is no additional salvation or protection. This situation is created by increasing the solvent power of the solvent e.g. by using a mixture like DMF – water mixture as solvent in place of a pure solvent.

Application of empirical relation to the data:

The empirical relation is,

$$\eta_{sp/c} = Z = [\eta] + \frac{K[\eta]}{C^{1/2}}$$

The application of the equation to the data has been examined and the results are represented in the **Table 5**. The plots are shown in **Figure 3**; this was indicated that the plots were linear. From the plots, values of intercept [ƞ] and K were appraised. These constants are presented in table 5. The above mentioned empirical equation is able to represent the empirical data for all the oligoimides. It may be stated that as the equation is quite empirical, no significance can be attached to the definition of the intercept which follows from the equation.

Table 1: Structure of OIs

Oligoimides	Designation	Molar ratio of CMOI
1	OI-1	1:2
2	OI-2	1:1.75
3	OI-3	1:1.50
4	OI-4	1:1.25

Table 2: Structure of CMOI

Oligoimide sample	Designation	Molar ratio of CMOI
1	CMOI-1	1:2
2	CMOI-2	1:1.75
3	CMOI-3	1:1.50
4	CMOI-4	1:1.25

Table 3: Reduce viscosity of solution of CMOIs using DMF.

Oligoimides	Reduced Viscosity (η_{red}dL/g) at concentration, (C g/dL)				
	3.000	**2.142**	**1.666**	**1.363**	**1.152**
CMOI-1	0.56172	0.56136	0.56400	0.57900	0.59028
CMOI-2	0.71040	0.69744	0.70500	0.71724	0.77232
CMOI-3	0.64560	0.62448	0.64920	0.68928	0.71772
CMOI-4	0.48540	0.49164	0.50076	0.53760	0.55152

Table 4: Reduce viscosity of solution of CMOIs using DMF-water-KBr (80:20:1%).

Oligoimides	Reduced Viscosity (η_{red}dL/g) at concentration, (C g/dL)					Intrinsic Viscosity [η]x10^2	Slop of linear plot K x10^3
	3.000	**2.142**	**1.666**	**1.363**	**1.152**		
CMOI-1	0.45096	0.45672	0.47124	0.48168	0.50172	47.2	27.36
CMOI-2	0.55464	0.57012	0.58272	0.59004	0.6036	58.0	24.05
CMOI-3	0.48996	0.4944	0.49896	0.50724	0.52044	50.2	16.35
CMOI-4	0.35196	0.35088	0.35388	0.35892	0.36768	35.7	9.21

Table 5: Reduce viscosity of solution of CMOIs using DMF.

Oligoimides	Reduced Viscosity (η_{red}dL/g) vs $1/C^{1/2}$					Intrinsic Viscosity [η] x 10^2
	0.577	**0.683**	**0.774**	**0.856**	**0.931**	
CMOI-1	0.56172	0.56136	0.56400	0.57900	0.59028	57.13
CMOI-2	0.71040	0.69744	0.70500	0.71724	0.77232	72.00
CMOI-3	0.64560	0.62448	0.64920	0.68928	0.71772	66.53
CMOI-4	0.48540	0.49164	0.50076	0.53760	0.55152	51.34

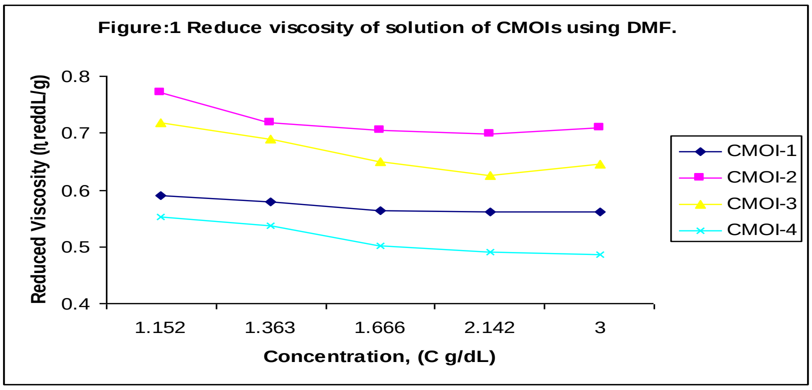


Figure:1 Reduce viscosity of solution of CMOIs using DMF.

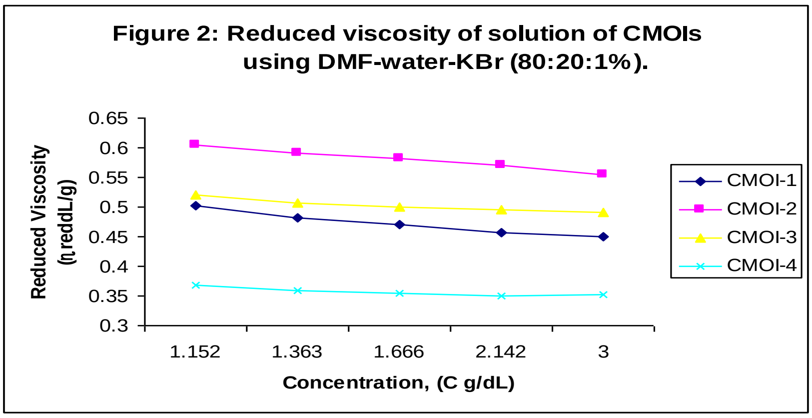
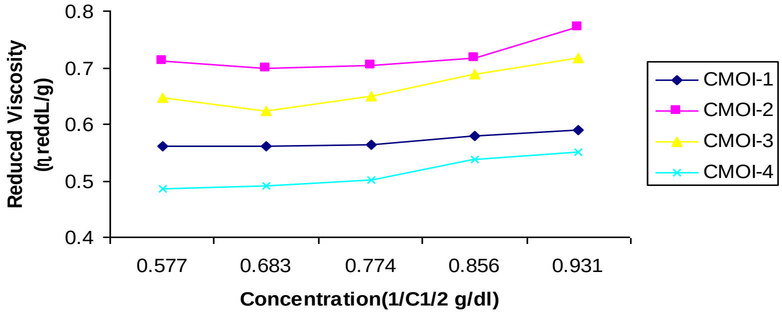


Figure 2: Reduced viscosity of solution of CMOIs using DMF-water-KBr (80:20:1%).

Figure 3: Reduced Viscosity vs 1/C1/2 of CMOIs (Application of empirical relation).



CONCLUSION

The intrinsic viscosity has been determined by extrapolating the reduced viscosity to zero concentration. The effects of solvent DMF, solvent-water, and solvent-water-KBr on viscosity have been investigated. It was shown that the reduced viscosity of DMF using solution of CMOI as a result of oligoimide chain expansion increases with decreasing oligoimide concentration. In fact the oligoimide behaves like a polyelectrolyte in salt-free solution. The effect of water on reduced viscosity was studied and it was found that reduced viscosity decreases with the mixing of water content in to the solvent. Adding of low molecular weight electrolyte (KBr) to the oligoimide solution eliminates the polyelectrolyte effect and oligoimide behaves like a neutral macromolecule. The viscosity decreases with decrease the oligoimide concentration, which is usually observed in neutral oligoimides.

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