Research Paper

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Viscometric Study of Carboxymethyl Epoxy resin based polyesters

Chemistry

KEYWORDS : Polyelectrolyte, Polyester epoxy resin, Ubbelohde viscometer, reduced viscosity, empirical relation and intrinsic viscosity.

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ABSTRACT

Various Epoxy resin based polyesters were prepared by reported method. The carboxymethylation of this polyester was claimed out by their reaction with mono chloro acetic acid. The resultant carboxymethylated polyesters (CMPEs) were characterized. The viscosity measurement of solutions of all CMPE was calmed out in DMF at 35+ 0.1oC. The ubbelohde suspended type viscometer was used for such measurement. The viscosity data of the solution of CMPE resins signified that the decrease in concentration of solution increases reduced viscosity (ηred). This suggests the CMEF resins 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 CMPE resins in DMF-Water-KBr (80:20:1%) gives the intrinsic viscosity. Also applying empirical equation

[illegible]

is able to represent the viscometric data for all the resins. It may be stated that as the equation is quite empirical.

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 polyester resins derived from epoxy-resin and bis-acids are reported in literature [10]. Their modification by carboxymethylation has not been reported. It such derivation of such polyster is carried out, the resultant polymer may act as polyelectrolyte. So the present communicant comprises the synthesis, characterization and study of solution properties of carboxymethylated epoxy-resin polyester resins. The work is shown in **Scheme 1**.

Experimental:

Materials:

Epoxy resin based polyster resin were prepared by reported method [10].All of the chemical used were of pure grade. The viscometer bath was used with maintaining temperature 30º ± 0.3ºC.

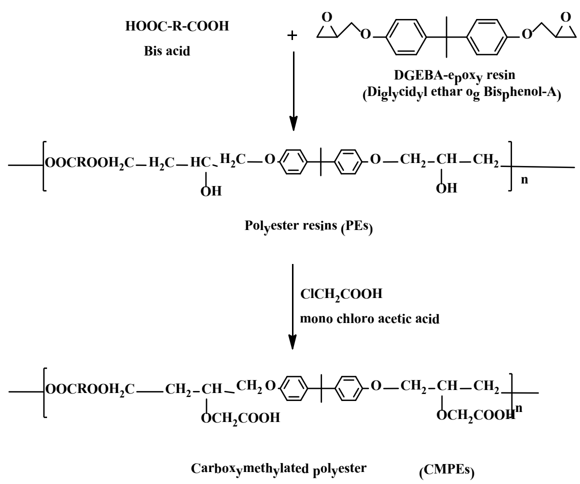
Table 1: Structure of PE resin

Polymer sample	PE resin	R
1	PE-1	-
2	PE-2	$-CH_2$
3	PE-3	$-(CH_2)_2-$
4	PE-4	$-(CH_2)_4-$

Synthesis of Carboxymethyl PE resins:

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

To a solution of PE resins (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 mono chloro acetic acid in water added stoichiometrcally. The solid precipitates of carboxy methyl PE resin was obtained, filtered, washed by petroleum ether and air dried. The products were designated as CMPE- 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 CMPEs

Table 2: Structure of CMPE resin

Polymer sample	Designation	Structure of CMPE resin
1	CMPE-1	-
2	CMPE-2	$-CH_2$
3	CMPE-3	$-(CH_2)_2$
4	CMPE-4	$-(CH_2)_4-$

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Measurements:

The non-aqueous conductometric titration of all the CMPEs was carried out in pyridine against standard tetra-n-butyl ammonium hydroxide in pyridine as titrate**.** The number average molecular weight of all the four CMPEs was estimated by Vapour Pressure Osmometer (VPO) Knauer K7000 in DMF at 70º ± 0.1ºC **(Table-3)**.The infrared spectra (FT-IR) were obtained from KBr pellets in the range 4000–400 cm^{-1} with a Perkin Elmer spectrum GX spectrophotometer (FT–IR) instrument. The thermogravimetric analysis of CMPEs was carried out by Du Pont 950 thermogravimetric analyzer at 10°K per minutes.

The relative, specific and reduced viscosity of the CMPE resin 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 30º ± 0.3ºC. 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 polymer solutions against concentration (g/dL), extrapolating to infinite dilution and taking the intercept, the intrinsic viscosity [η] is determined.

Table 3: Non-aqueous conductometric titration and Num. verage molecular weight Mn by VPO.

Resins	**Non-aqueous conductometric titration mmol of –COOH /100gm**	**Mn by VPO in DMF at 70º ± 0.1ºC. ±20**
CMPE-1	26.82	650
CMPE-2	24.72	720
CMPE-3	21.46	800
CMPE-4	20.01	850

Table 4: Reduce viscosity of solution of CMPE resin using DMF.

Polymer Samples	**Reduced Viscosity (η_{red}dL/g) at concentration, (C g/dL)**				
	3.000	2.142	1.666	1.363	1.152
CMPE-1	0.09362	0.09256	0.0940	0.0965	0.09838
CMPE-2	0.11840	0.11624	0.1175	0.11954	0.12872
CMPE-3	0.10670	0.10408	0.1082	0.11488	0.11962
CMPE-4	0.08090	0.08194	0.08346	0.08960	0.09192

Table 5: Reduce viscosity of solution of CMPE resin using DMF-water-KBr (80:20:1%).

Polymer Samples	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		
CMPE-1	0.08362	0.08028	0.07854	0.07612	0.07516	7.02	4.56
CMPE-2	0.1006	0.09834	0.09712	0.09502	0.09244	8.92	4.01
CMPE-3	0.08674	0.08454	0.08316	0.0824	0.08166	7.86	2.72
CMPE-4	0.06128	0.05982	0.05898	0.05848	0.05866	5.65	1.54

Table 6: Reduce viscosity of solution of CMPE resin using DMF.

Polymer Samples	**Reduced Viscosity (η_{red}dL/g) vs 1/$C^{1/2}$**					**Intrinsic Viscosity [η]x10^2**
	0.577	0.683	0.774	0.856	0.931	
CMPE-1	0.09362	0.09256	0.0940	0.0965	0.09838	9.71
CMPE-2	0.11840	0.11624	0.1175	0.11954	0.12872	11.3
CMPE-3	0.10670	0.10408	0.1082	0.11488	0.11962	9.45
CMPE-4	0.08090	0.08194	0.08346	0.89600	0.09192	6.53

Figure 1: Reduced Viscosity vs Concentration of CMPE resins using DMF.

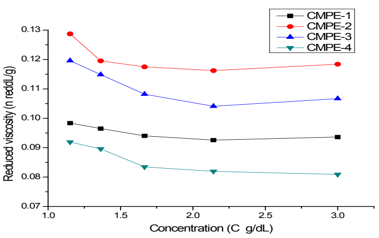


Figure 2: Reduced Viscosity vs Concentration of CMPE resins using DMF -water-KBr (80:20:1%).

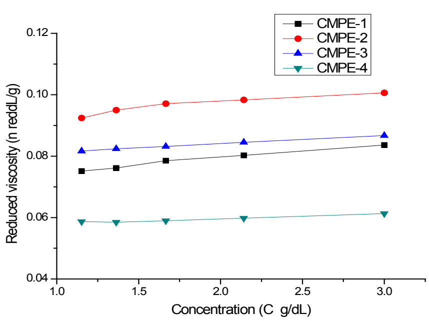
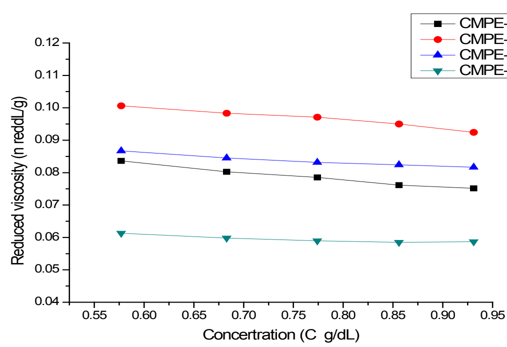


Figure 3: Reduced Viscosity vs 1/$C^{1/2}$ of CMPE (Application of empirical relation).



Results and Discussion:

All the four resins i.e. CMPE 1 to 4 were in form of amorphous power. The non-aqueous conductometric titrations of all the resins require mmoles of sodium methanolate per 100g sample for neutralization. These are showing **Table-3**. The data suggest that the value is consistent with the structure. The number average molecular weight Mn of all the four resins is in the rage of 650 to 850 depending of the nature of polymer. The IR spectra of all the resins are almost identical in shape and intensity of bands. Only discernible band are 1720cm^{-1} is responsible to –COOH group.

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The reduced viscosity of the CMPE resin solution in to the DMF solvent is shown in **Figure 1** as the function of polymer concentration. It is seen from the **Figure 1** that the reduced viscosity increases with the decreasing polymer concentration. This typical polyelectrolyte behavior like this for the reason that the carboxylic groups on the polymer chain can ionize in the polar solvent and also the effective electrostatic repulsion makes this polymer 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 polymers have special viscosity behavior in association with neutral polymer. Neutral polymers have the properties that reduce viscosity increases with the increase of polymer 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 polymer 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 polymer concentration, which is in contrast with salt-free solution.

Viscosity of a given solution of a rigid polymer depends upon the interactions between the polymer chain and upon the hydrodynamic volume of the polymer. In the present case the solution contains a polycarboxylate ion. Because of lower shielding of the COO^- ions present in the polymer chains, the polymer chains will keep away from each other to minimize the repulsive interaction. With increase in dilution, the number of solvent molecules per molecules of polymer chain would increase. Hence number of solvent molecules surrounding each ion on polymer chain would increase. The repulsive interaction of polymer 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 polymer 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,

The application of the equation to the data has been examined and the results are represented in the **Table 6**. The plots are shown in **Figure 3**; this was indicated that the plots were linear. From the plots, values of intercept [η] and K were appraised. These constants are presented in table 6. The above mentioned empirical equation is able to represent the empirical data for all the polymers. 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.

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 CMPE resins as a result of polymer chain expansion increases with decreasing polymer concentration. In fact the polymer 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 polymer solution eliminates the polyelectrolyte effect and polymer behaves like a neutral macromolecule. The viscosity decreases with decrease the polymer concentration, which is usually observed in neutral polymers.

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