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Green analytical methods for determination of intrinsic viscosity of hydroxyl terminated polybutadiene

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Abstract

In this work, determination of intrinsic viscosity, $[\eta]$, of HTPB polymers (synthesized by free radical as well as anionic polymerization) was carried out by single point methods which are environmental benign as they use relatively less solvent than the classical methods. Five different methods were studied to select the best one for fast and accurate determination of $[\eta]$ of HTPB for routine quality control application. The polymer-solvent interaction parameter (χ) in three different solvents, i.e. toluene, tetrahydrofuran, and chloroform, was evaluated to select the suitable solvent for this study. Two approaches, i.e. Hoftyzer-Van Krevelen and Hoy, were used for estimation of solubility parameter (δ_{HTPB}) of the polymers. The δ_{HTPB} obtained by Hoftyzer-Van Krevelen method was found to deviate slightly from Hoy's method. The average value of δ_{HTPB} was 17.25 and 16.77 MPa$^{1/2}$ for free radical and anionic-HTPB respectively. The $\Delta\delta$ value (difference between solubility parameters of polymer and solvent) was in the order: toluene < chloroform < tetrahydrofuran. The χ value in toluene was the lowest (i.e. 0.38) indicating good solvation of the polymer. The results of $[\eta]$ in toluene at 30 ± 0.1 °C obtained by single point methods were compared with the value obtained by graphical extrapolation methods based on Huggins, Kraemer, Martin, and Schulz-Blaschke equations. The Huggins constant (k_H) was < 0.4 for both the polymers. The single point method based on Kuwahara was found to be the best alternative to the graphical extrapolation methods with a deviation of ± 0.1 % from the value obtained by Huggins method. The proposed method would save approximately 80 % solvent used as well as labour and time. Thus, it is the most economical and environmental benign method for determination of intrinsic viscosity of HTPB polymer.

Keywords: HTPB, intrinsic viscosity, viscometry, green-analytical-method, solubility-parameter.

1. Introduction

Intrinsic viscosity, $[\eta]$, is one of the key parameters required to evaluate rheological properties of polymers. It gives information on fundamental properties of the solute (polymer) and its interaction with the solvent. It can be precisely related to the conformation of flexible chain (linear & non-linear), wormlike macromolecules and micelles, and rigid particles of arbitrary shape [1].

The concentration dependence on viscosity of a polymer solution can be expressed by Taylor expansion [2] written as:

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2 c + k_2[\eta]^3 c^2 + k_3[\eta]^4 c^3 + \cdots + k_n[\eta]^{n+1} c^n \qquad (1)$$

where η_{sp} is the specific viscosity and c, k_i, and $[\eta]$ are the concentration, constant, and intrinsic viscosity of the polymer respectively. The viscosity of the polymer solution is usually determined from the efflux time of pure solvent (t_o) and the polymer solution (t_p) in a capillary viscometer. These effluxes time are proportional to the viscosities of the polymer solution (η_p) and pure solvent (η_o). The intrinsic viscosity is defined as: $[\eta] = \lim_{c\to 0} \eta_{sp}/c$, where c is the concentration of the polymer solution (g/dL or g/cm^3) and $\eta_{sp} = \eta_r - 1$[1].

The relative viscosity (η_r) is defined as: $\eta_r = \eta_p/\eta_0$. At sufficiently dilute polymeric solution, the higher terms in Eq.(1) can be neglected. Thus, it would take the form:

$$\eta_{sp}/c = [\eta]_H + k_H[\eta]_H^2 c \qquad (2)$$

This equation is widely known as Huggins equation [3]. The constant k_H is the Huggins constant and $[\eta]_H$ is the intrinsic viscosity with respect to the Huggins equation. A number of empirical equations have been derived from Eq.1 for experimental determination of $[\eta]$ for various polymers. The most commonly used methods are Huggins, Kraemer, Martin, and Schulz-Blaschke [4]. All these classical methods are based upon linear graphical extrapolation of experimental data (GEED).The procedure for determination of $[\eta]$ for a polymer consists of measuring the viscosities of polymer solutions at different concentrations (c) and plotting η_{sp}/c against c of the polymer. The intercept of the linear least square regression plot of η_{sp}/c vs. c gives the value of $[\eta]_H$. For accurate determination of $[\eta]$, at least five dilute polymeric solutions in a good solvent are required.

The $[\eta]$ value of HTPB polymer is traditionally determined by Huggins graphical extrapolation method. This method is found to be very laborious and time consuming specially when used in routine quality control analysis as it involves large number of polymeric solutions. Of late, the inconvenience of extrapolation in routine analysis has drawn considerable interest on methods that are simple, fast, and reliable known as single point method of evaluation (SPME). Over the years, different methods of SPME, e.g. Solomon and Ciuta, Deb and Chatterjee, Rao and Yanseen, Kuwahara, and Palit and Kar, have been developed which eliminate the concentration dependence [5]. These are found to be excellent analytical tools in industrial quality control laboratory for estimation of $[\eta]$of polymers. Additionally, they are environmental benign methods as less amount of solvent is used. The current trend in industrial research and development is the application of green chemistry rules in designing greener analytical methods that are simple, fast, and reliable as compared to the classical methods. Recently, SPME methods have been successfully applied by Mellow *et al.* for determination of $[\eta]$of high-cis polybutadiene [6]. Ghose *et al.* studied the applicability of these methods in homopolymer of methyl methacrylate and its copolymer with styrene and 1-decene [7]. However, the validity of these methods for HTPB polymer has not yet been studied and requires to be explored.

The aim of present study was to determine the value of $[\eta]$ for HTPB in a suitable solvent by SPME methods with reference to the conventional graphical extrapolation (GEED) methods and evaluate the validity of these SPME methods for fast and reliable estimation of $[\eta]$ of HTPB for industrial quality control application.

2. Experimental

2.1. Materials

Two types of hydroxyl terminated polybutadiene (HTPB), i.e. free radical and anionic-HTPB, have been used in the present study. Free radical-HTPB (NOCIL, India) had the hydroxyl value = 43 mg KOH/g, polydispersity = 2.1, viscosity at 30 ºC = 6000 mPa.s, and viscosity at 60 ºC = 1590 mPa.s. Anionic-HTPB (KRASOL, USA) had the hydroxyl value = 50 mg KOH/g, polydispersity = 1.8, viscosity at 30 ºC = 8200 mPa.s, and viscosity at 60 ºC = 900 mPa.s.

2.2. Methods

2.2.1. Calculation of polymer-solvent interaction parameter in different solvents.

The polymer-solvent interaction parameter (χ) in three different solvents, i.e. toluene, tetrahydrofuran, and chloroform, was evaluated to select the suitable solvent for this study. According to Flory-Huggins [8, 9], the value of χ can be calculated as :$\chi = 0.34 + (V_s/RT)(\delta_{poly} - \delta_{sol})^2$,where δ_{poly} and δ_{sol} are the solubility parameters of polymer and solvent respectively, V_s is the molar volume of solvent, R is the gas constant, and T is the absolute temperature. Hansen solubility parameters (HSP) of HTPB polymers were calculated by Hoftyzer-Van Krevelen as well as Hoy's method [10] which are based upon dispersive forces, i.e. $\delta_d = \sum F_{di}/V$, the polar forces, i.e. $\delta_p = \left(\sum F_{pi}^2\right)^{0.5}/V$, and the hydrogen component, i.e. $\delta_h = (\sum E_{hi}/V)^{0.5}$, where F_{di}, F_{pi}, and E_{hi} are the intrinsic properties related to their structural groups. The total solubility parameter (δ_t) is given as: $\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$. The average value of the results obtained by these two methods has been reported as solubility parameter of HTPB polymer.

2.2.2. Intrinsic viscosity measurement

Intrinsic viscosity measurements were carried out at 30 ± 0.1 °C using an Ubbelohde viscometer. Five different concentrations, i.e. 0.25, 0.50, 0.75, 1.0, and 1.25 g/dL, were prepared from 2.0 g/dL of polymer stock solution in toluene. The efflux times of the polymer solutions were determined by a chronometer. Each run time was repeated three times, and the average value was taken for calculation.

2.2.3. Determination of [η] and viscometric parameters by GEED

In GEED methods, Huggins (Eq.2), Kraemer (Eq.3), Martin (Eq.4), and Schulz-Blaschke (Eq.5) [4] were used to determine the dilute solution properties of HTPB polymers.

$$\ln\eta_r/c = [\eta]_k - k_k[\eta]_k^2 c \qquad (3)$$
$$\ln(\eta_{sp}/c) = \ln[\eta]_m + k_m[\eta]_m c \qquad (4)$$
$$\eta_{sp}/c = [\eta]_{sb} + k_{sb}[\eta_{sb}]\eta_{sp} \qquad (5)$$

where $[\eta]_k$= intrinsic viscosity with respect to Kraemer equation, $[\eta]_m$ = intrinsic viscosity with respect to Martin equation, and $[\eta]_{sb}$= intrinsic viscosity with respect to Schulz-Blaschke equation. The constants, i.e. k_k, k_m, and k_{sb} are Kraemer, Martin, and Schulz-Blaschke coefficient respectively.

2.2.4. Determination of [η] by SPME

In single point methods, the Solomon and Ciuta (Eq.6), Deb and Chatterjee (Eq.7), Rao and Yanseen (Eq.8), Kuwahara (Eq.9), and Palit and Kar (Eq.10) [5] were used for estimation of $[\eta]$ of HTPB polymers.

$$[\eta] = [2(\eta_r - 1 - \ln\eta_r)]^{0.5}/c \qquad (6)$$
$$[\eta] = \left(3\ln\eta_r + 3/2\eta_{sp}^2 - 3\eta_{sp}\right)^{1/3}/c \qquad (7)$$
$$[\eta] = \left(\eta_{sp} + \ln\eta_r\right)/2c \qquad (8)$$
$$[\eta] = \left(\eta_{sp} + 3\ln\eta_r\right)/4c \qquad (9)$$
$$[\eta] = \left(4\eta_{sp} - 4\ln\eta_r + 1.33\eta_{sp}^3 - 2\eta_{sp}^2\right)^{1/4}/c \qquad (10)$$

3. Results and discussion

3.1. Polymer-solvent interaction parameter of HTPB.

To select a good solvent for this study, we determined the mutual solubility of HTPB polymer in three different solvents, i.e. toluene, tetrahydrofuran, and chloroform. The solubility of a polymer can be defined by polymer-solvent interaction parameter (χ) given by Flory-Huggins [11]. According to Flory-Huggins model, the polymer and the solvent are completely miscible, if $\chi < 0.5\left(1 + \left(V_s/V_p\right)^{0.5}\right)^2$, where V_s and V_p are the molar volume of solvent and polymer respectively. The number average molecular weights of HTPB polymers (i.e. 5891 g/mol for free radical and 4068 g/mol for anionic-HTPB) were very high as compared to the solvents used, which implies that $V_p >>> V_s$.Therefore, the criterion for complete solvent-polymer miscibility would be $\chi \leq 0.5$.

A good solvent implies that the solvent has more affinity towards the polymer, i.e. the polymer-solvent interaction is more than the polymer-polymer and solvent-solvent interactive forces. The more the polymer-solvent interaction, better will be the dissolution of the polymer. The dissolution of the polymer depends upon many factors, e.g. the molecular weight, polydispersity, structure, composition, conformation of the polymer chain etc [12]. Fig. 1 shows the chemical structure of HTPB obtained by free radical and anionic polymerization method.

As seen in Fig.1, the polymer backbone of HTPB consists of –CH=, -CH_2-, -CH<, and =CH_2 groups, and the olefinic groups are present in three different configurations, i.e. *trans*-1, 4-units(α), *vinyl*-1, 2-units(β), and *cis*-1, 4-units (γ). The relative content of α, β, and γ were determined by high filed NMR spectroscopic method and reported elsewhere [13]. The free radical HTPB has 19.4% of *cis*-1,4-units, 59.6 % of *trans*-1,4-units, and 21.0 % of *vinyl*-1,2-units whereas the anionic HTPB has 9.7 % of *cis*-1,4-units, 21.9 % of *trans*-1,4-units, and 68.4 % of *vinyl*-1,2-units in its backbone.

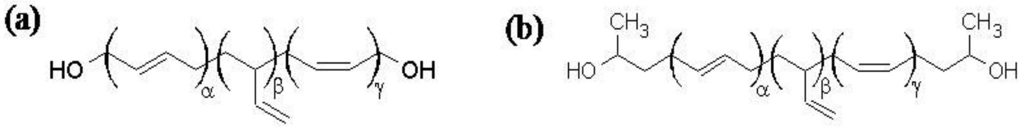

Figure1: Molecular structure of HTPB (a) Free radical-HTPB, and (b) Anionic-HTPB polymer (the α, β, and γ are the *trans*-1, 4-, *vinyl*-1, 2-, and *cis*-1, 4-content respectively).

According to Flory-Huggins, the values of solubility parameter (δ) of HTPB polymer as well as the solvent are required for determination of χ . By definition, the solubility parameter is equal to the square root of cohesive energy density. Cohesive energy is determined from enthalpy of vaporization of the polymer [14]. However, for HTPB polymer, there is no measurable value of enthalpy of vaporization or boiling point. Therefore, we used group contribution methods for calculation of solubility parameter of HTPB polymers. For HTPB polymer, each isomer (α, β, and γ as shown in Fig.1) will contribute to the total energy of vaporization as well as to the molar volume of the polymer according to its percentage [14]. In order to get the total energy of vaporization and molar volume of the HTPB polymer, the energy of vaporization and molar volume of each individual isomer was calculated and multiplied by their respective fractions, and then, the solubility parameter of the polymer was calculated. Two different methods, i.e. Hoftyzer-Van Krevelen and Hoy's method, were used for determination of solubility parameter of HTPB polymers. Table 1 lists the various parameters calculated in three different solvents.

Table 1: Solubility and polymer-solvent interaction parameters for free radical and anionic HTPB polymers.

Parameter	Solvent			Polymer	
	Toluene	THF	Chloroform	Free radical #/*	Anionic #/*
V(cm^3/mol)	106.8	81.7	80.7	57.46/57.46	150.78/150.72
δ_d(MPa)$^{1/2}$	18.0	16.8	17.8	16.40/17.17	16.49/16.65
δ_p (MPa)$^{1/2}$	1.4	5.7	3.1	0.0/5.64	0/3.63
δ_h(MPa)$^{1/2}$	2.0	8.0	5.7	0.0/1.15	0.0/0.0
δ_t(MPa)$^{1/2}$	18.2	19.5	18.9	16.40/18.11	16.49/17.04
Δδ/Free radical-HTPB	2.9	9.8	6.6	---	---
Δδ/Anionic-HTPB	2.9	9.8	6.6	---	---
χ /Free radical-HTPB	0.38	0.50	0.43	---	---
χ /Anionic- HTPB	0.43	0.58	0.50	---	---

\# Hoftyzer-Van Krevelen and *Hoy's method

The solubility parameter (δ_t) obtained by Hoftyzer-Van Krevelen method was found to slightly deviate from Hoy's method. The deviations between the two arithmetic methods were found to be ≤ 9 %. According to Van Krevelen, the safest way to estimate the solubility parameter is to take the average value of the results obtained from both the methods [10]. The average value of solubility parameter was found to be 17.25 and 16.77 MPa$^{1/2}$ for free radical and anionic-HTPB respectively. The polymer tends to be well dissolved in a solvent when the solubility parameters of the polymer and solvent are close to each other [10].Therefore, the difference of solubility parameters (i.e. $\Delta\delta$ value) can be used to predict the mutual solubility between polymer and solvent. It could be determined as: $\Delta\delta^2 = \left(\delta_{d(poly)} - \delta_{d(sol)}\right)^2 + \left(\delta_{p(poly)} - \delta_{p(sol)}\right)^2 + \left(\delta_{h(poly)} - \delta_{h(sol)}\right)^2$. For good solubility, the $\Delta\delta$ value should be less than 5 MPa$^{1/2}$. In Table 1, it could be seen that the $\Delta\delta$ as well as χ values were in the order: toluene < chloroform < tetrahydrofuran for both the HTPB polymers. The $\Delta\delta$ value in toluene was 2.9 MPa$^{1/2}$ whereas in chloroform and tetrahydrofuran, it was found to be 6.6 and 9.8 MPa$^{1/2}$ respectively. Further, we found the value of χ in toluene is less than 0.5.This showed that among the three solvents studied, toluene met the criteria of a good solvent. Therefore, it was selected for studying the intrinsic viscosity of HTPB polymers.

3.2. Defining the limit of concentration for evaluation of [η].

In dilute solution, polymer molecules are relatively free to move independently. As the concentration increases, the polymer molecules get twisted and inter-penetrated each other to form entanglements. This transition occurs at a particular concentration called critical concentration (c^*). Above the critical concentration, the flow properties of the polymer change due to the formation of entanglements among the polymer molecules [15]. Therefore, the critical concentration represents the upper limit for study of dilute solution behavior of the polymer. In this study, we selected the concentration of HTPB polymers in the range from 0.25 to 1.25 g/dL. To check whether molecular entanglements were formed or not within the selected range of concentrations, we plotted the values of $\ln \eta_{sp}$ against $\ln c[\eta]_H$. The $c[\eta]$ value represents the volumetric portion occupied by the polymeric chain in dilute solution, and it is related to the specific viscosity of the polymer solution by the equation as follows: $\eta_{sp} = K(c[\eta])^m$, where m is the slope of the plot of $\ln \eta_{sp} vs.\ \ln c[\eta]$. All the polymer concentrations would correspond to the dilute domain, when a good linearity in the plot of $\ln \eta_{sp} vs.\ \ln c[\eta]$ is observed [6]. Fig. 2 shows the plots of $\ln \eta_{sp} vs.\ \ln c[\eta]_H$ for both the polymers under investigation. It was observed that within the concentrations range studied, there was no change in slope of the curves. The slopes of the regression lines were found to be 1.022 and 1.030 for anionic and free radical polymer respectively with correlation coefficients of unity. This showed that all the polymeric solutions under study were in dilute domain ($c < c^*$) and therefore, valid for study the dilute solution properties of HTPB polymers.

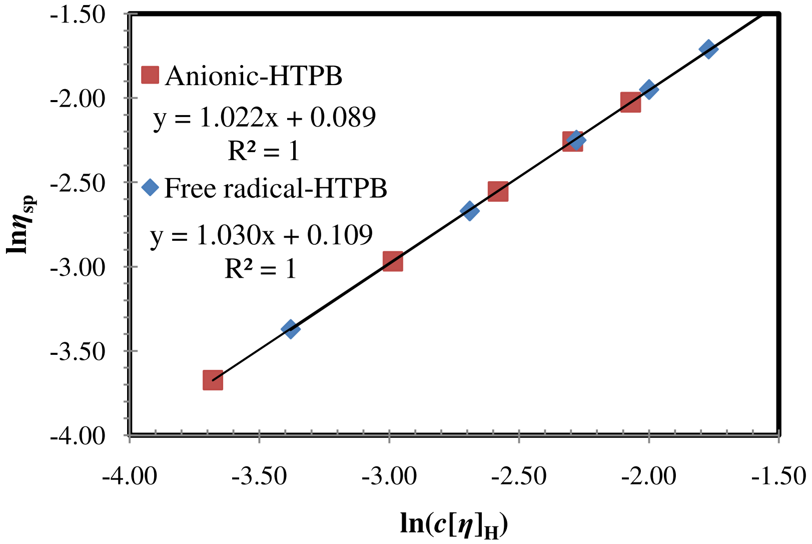

Figure 2: The plots of $\ln \eta_{sp} vs.\ \ln c[\eta]_H$ for free radical and anionic HTPB polymers.

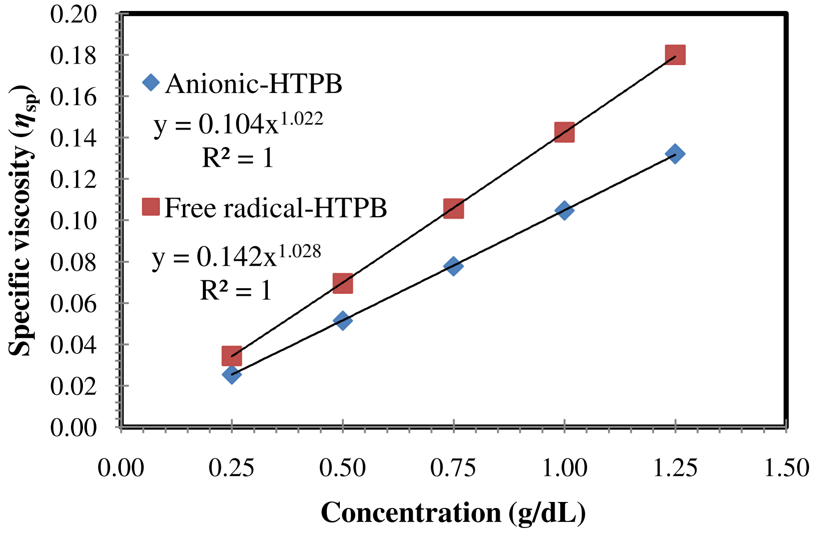

Figure 3: Power law plots for free radical and anionic HTPB polymers.

This conclusion was further supplemented from the relationship between the specific viscosity and the concentration which can be expressed by the power law equation as follow:

$$\eta_{sp} = ac^n \qquad (11)$$

The power law index (n) predicts the conformation of a polymeric chain in dilute solution. It is reported that the value of power index less than unity is associated with rod like conformation and greater than unity is associated with random coil conformation or entanglement [16]. Fig. 3 shows the power law plots for both the polymers. The power law index (n) in both the polymers were found to be close to unity. This indicated that random-coil like conformations were insufficient to form entanglement in solution of both free radical as well as anionic polymer. Further, it was also seen in Fig.2 that the slopes of both the regression lines of $\ln \eta_{sp}$*vs.* $\ln c[\eta]_H$ plots were close to unity and more or less matched with the value of power law index. This further confirmed that no molecular entanglements were obtained in the concentration range studied, and all the solutions were truly diluted and obeyed the Huggins law in the limit of zero concentration.

3.3. Intrinsic viscosity by graphical extrapolation methods.

The specific viscosities of the polymeric solutions were obtained at different concentration ranging from 0.25 to 1.25 g/dL, and the intrinsic viscosities were determined by graphical extrapolation as per Huggins, Kraemer, Martin, and Schulz-Blaschke equations. Table 2 lists the value of $[\eta]_i$ and various viscometric constants (k_i) for free radical and anionic-HTPB obtained by graphical methods.

The $[\eta]_i$values obtained by different graphical extrapolation methods were found to be nearly same. The $[\eta]_H$ and $[\eta]_K$ were found to be same indicating agreement between the Huggins and Kraemer models. The Huggins constant (k_H) is a measure of polymer-polymer interactions in solution. The higher the affinity between polymer and solvent molecules, the lower would be the value of k_H. For good solvent, the value falls in the range of 0.30-0.40, and for θ-solvent, it is 0.5-0.80 [17]. We found the value of k_H to be less than 0.4 for both the polymers. This showed that the quality of solvent used was good which was further supplemented by Kraemer constant. The low values of k_K indicated good polymer solvation.

3.4. Intrinsic viscosity by single point methods.

In single point methods of evaluation (SPME), intrinsic viscosity is determined from the single value of concentration. Thus, these methods avoid the use of large amount of solvent and could be considered as green analytical methods. The SPME method like Solomon and Ciuta could be derived by combining the Huggins and Kraemer equations assuming k_H+ k_K= 0.5.Therefore, the Solomon and Ciuta method would be applicable if the Higgins as well as Kraemer method give the same value of $[\eta]$.

Table 2: The value of $[\eta]$ and viscometric constants for free radical and anionic- HTPB polymers obtained by different GEED methods.

Methods	Anionic HTPB ($\bar{M}_n$= 4068 g/mol)				Free radical HTPB ($\bar{M}_n$= 5891 g/mol)			
	Huggins	Kramer	Martin	Schulz-Blaschke	Huggins	Kramer	Martin	Schulz-Blaschke
Conc.(c) in g/dL	η_{sp}/c	$\ln \eta_r/c$	$\ln(\eta_{sp}/c)$	η_{sp}/c	η_{sp}/c	$\ln \eta_r/c$	$\ln(\eta_{sp}/c)$	η_{sp}/c
0.25	0.1017	0.1005	-2.2855	0.1017	0.1377	0.1354	-1.9829	0.1377
0.50	0.1029	0.1004	-2.2738	0.1029	0.1390	0.1343	-1.9736	0.1390
0.75	0.1037	0.0999	-2.2658	0.1037	0.1409	0.1340	-1.9596	0.1409
1.0	0.1047	0.0996	-2.2565	0.1047	0.1426	0.1333	-1.9478	0.1426
1.25	0.1057	0.0992	-2.2475	0.1057	0.1440	0.1324	-1.9380	0.1440
$[\eta]$ (dL/g)	0.1009	0.1009	0.1009	0.1009	0.1359	0.1360	0.1360	0.1361
Constant	k_H =0.3831	k_K =0.1277	k_M =0.3697	k_{SB} =0.3598	k_H =0.3519	k_K =0.1514	k_M =0.3397	k_{SB} =0.3284
r^2	0.997	0.974	0.997	0.996	0.996	0.983	0.996	0.996

In Table 2, it was seen that the $[\eta]$ value obtained by Huggins method was same as that of Kraemer method, which implied that Solomon and Ciuta method would be valid for the HTPB/toluene system. However, in general, the $[\eta]$ value obtained by Solomon and Ciuta method deviates based on the polymer concentration for a particular polymer/solvent system, and the relative deviation in $[\eta]$ with reference to Huggins value defined as: $([\eta]_i - [\eta]_H)/[\eta]_H$ would be zero when k_H=0.33[1]. It could be seen in Table 2 that in both anionic and free radical-HTPB, the value of k_H was in the range 0.3-0.4.This further revealed that the SPME methods could also be applied to HTPB/toluene system for estimation of $[\eta]$ with zero or negligible deviations.

Table 3: The value of $[\eta]$ of free radical and anionic-HTPB by different SPME methods.

Conc. (g/dL)	$[\eta]$ of Anionic HTPB (dL/g)					$[\eta]$ of Free radical HTPB (dL/g)				
	0.25	0.50	0.75	1.0	1.25	0.25	0.50	0.75	1.0	1.25
Solomon and Ciuta	0.1009	0.1012	0.1012	0.1013	0.1013	0.1361	0.1359	0.1362	0.1363	0.1362
Deb and Chatterjee	0.1011	0.1016	0.1018	0.1021	0.1024	0.1365	0.1366	0.1374	0.1379	0.1381
Rao and Yanseen	0.1011	0.1016	0.1018	0.1021	0.1025	0.1365	0.1367	0.1374	0.1379	0.1382
Kuwahara	0.1008	0.1010	0.1009	0.1009	0.1008	0.1359	0.1355	0.1357	0.1356	0.1353
Palit and Kar	0.0976	0.1001	0.1010	0.1017	0.1023	0.1332	0.1353	0.1369	0.1379	0.1385

Table 3 lists the values of $[\eta]_i$ of HTPB polymers obtained by five different SPME methods. It could be seen that the $[\eta]_i$ values obtained by different methods were more or less same with marginal deviation as compared to the Huggins value, which indicated the validity of these equations for estimation of intrinsic viscosity of HTPB polymers. Further, the $[\eta]_i$ values obtained at different concentrations by Deb and Chatterjee are close to the values obtained by Rao and Yanseen method. The $[\eta]_i$ values obtained by Deb and Chatterjee, Rao and Yanseen, and also Palit and Kar methods were found to be increasing with increase in concentration in both anionic and free radical-HTPB, and the value obtained at low concentration matched well with the value determined by GEED methods.

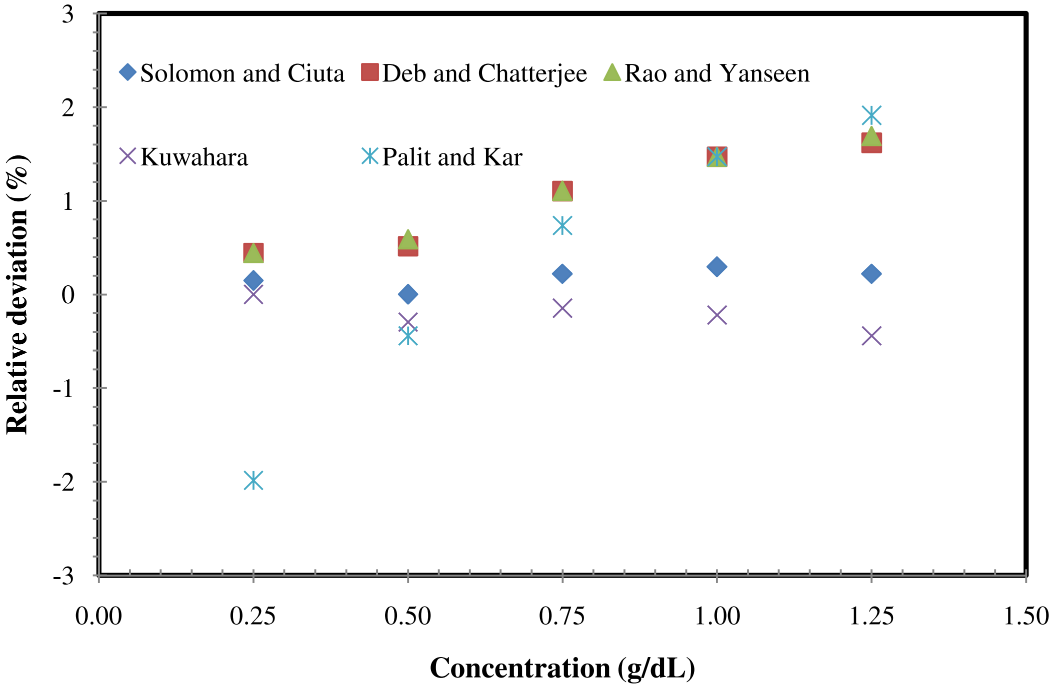

Figure 4: Plots of relative deviation (%) *vs*. concentration for free radical-HTPB.

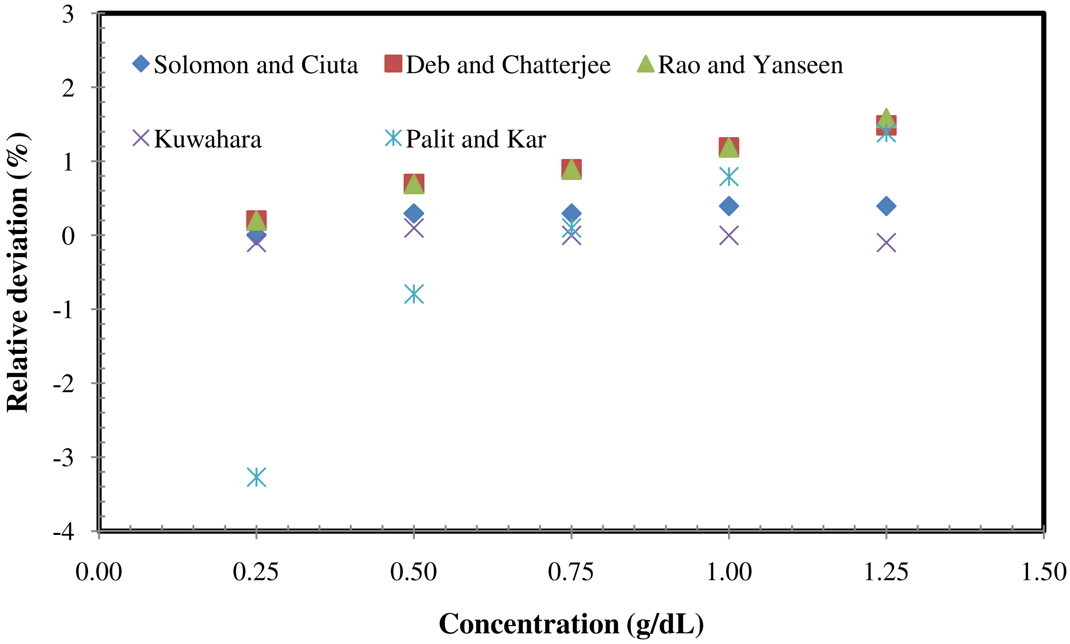

Figure 5: Plots of relative deviation (%) *vs*. concentration for anionic-HTPB.

To select the best SPME method for estimation of $[\eta]$ of HTPB polymers, the deviation of $[\eta]_i$ obtained at different concentration were calculated by taking Huggins value as reference. Figs. 4 and 5 show the plots of relative deviation (%) against concentration for free radical and anionic-HTPB respectively. We observed that in both the cases, the relative deviation (%) increased with increase in concentration. Lowest deviations (%) were observed in the dilute solution region. Further, Kuwahara method yielded the lowest deviations, i.e. ± 0.1 % (anionic-HTPB) within the concentration range studied.

Conclusion

The following conclusions were drawn from the present study:

1. The SPME methods were found to be excellent tool for determination of intrinsic viscosity of HTPB polymer. The main advantages are: (1) reduction of solvent (up to 80 %), (2) analysis time is less (1 hours to 30 mins/sample), (3) save energy as well as cost, and (4) less exposure time to solvents. Thus, these methods could be more economical as well as environmental benign method for determination of intrinsic viscosity.
2. The SPME method based on Kuwahara yielded the lowest deviation in order of ± 0.1 % as compared to the graphical Huggins method. Therefore, it could be considered as the best alternative to the graphical extrapolation method.
3. A large number of HTPB polymer samples could be easily, precisely, and rapidly analyzed by SPME, i.e. Kuwahara method, for intrinsic viscosity as compared to the linear extrapolation method. Therefore, this method would be the best aid for industrial quality control application of HTPB polymer.

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