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Viscometric study of high-*cis* polybutadiene in cyclohexane solution at 30°C

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Summary

High-*cis* polybutadiene solutions were prepared in cyclohexane at 30°C. Six different equations were used to calculate intrinsic viscosities and viscosimetric constant values from Huggins, Kraemer, Martin and Schulz-Blaschke equations by graphic extrapolation, and Solomon-Ciuta, Deb-Chantterjee and again Schulz-Blaschke equations, through a single point determination, which presents the advantage of being a faster method. The molecular mass of the polymers was determined applying Mark-Houwink-Sakurada equation. The values of intrinsic viscosity and viscosity-average molecular mass, obtained by both types of determination, were compared and the percentual differences between them were calculated in order to verify the validity of the single point determination for the system analyzed. The results suggest that the single point determination can be applied and Deb-Chantterjee equation showed to be the most suitable for those calculations.

Introduction

Viscometry is an appropriated method to provide some information about size and conformation of macromolecules in infinitely diluted solutions. A parameter directly related to that determination is the so called intrinsic viscosity [1,2].

Several mathematical equations are available in the literature [3-8] for determining the intrinsic viscosity [η] of a polymer solution, by graphical extrapolation (Equations 1 to 4) and from a single point viscosity measurement of a dilute solution (Equations 5 and 6).

$$\eta_{sp}/c = [\eta]_h + k_h\,[\eta]_h^2\,c \qquad (\mathbf{1})$$

$$\ln \eta_r/c = [\eta]_k - k_k\,[\eta]_k^2\,c \qquad (\mathbf{2})$$

$$\ln \eta_{sp}/c = \ln\,[\eta]_m + k_m\,[\eta]_m\,c \qquad (\mathbf{3})$$

$$\eta_{sp}/c = [\eta]_{sb} + k_{sb}\,[\eta_{sb}]\eta_{sp} \qquad (\mathbf{4})$$

$$[\eta]_{SC} = [2\,(\eta_{sp} - \ln \eta_r)]^{1/2} / c \qquad (\mathbf{5})$$

$$[\eta]_{DB} = (3 \ln \eta_r + 3/2\,\eta^2_{sp} - 3\,\eta_{sp}) / c \qquad (\mathbf{6})$$

where: $\eta_r = t/t_o$ is the relative viscosity or viscosity ratio (efflux time ratio between the solution, in a determined concentration, and the solvent); η_{sp} = specific viscosity ($\eta_{sp} = \eta_r - 1$); $[\eta]_h = \lim_{c\to 0} \eta_{red}$; $[\eta]_k = \lim_{c\to 0} \eta_{inh}$; $[\eta]_m = \lim_{c\to 0} \ln \eta_{red}$; $[\eta]_{sb} = \lim_{c\to 0} \eta_{red}$; $[\eta]_{SC;}$ $[\eta]_{DB}$ are the intrinsic viscosities related to Huggins, Kraemer, Martin, Shulz-Blaschke, Solomon-Ciuta and Deb-Chantterjee equations, respectively. k_h, k_k, k_m, and k_{sb} are Huggins, Kraemer, Martin and Schulz-Blaschke coefficients, respectively. For many polymer systems, $k_{sb} = 0.28$ has been found. In that way, that value is commonly employed in single point determinations, for many polymer systems. Huggins and Kraemer coefficients are related to chain conformation in the analysis conditions [9-13].

According to the Mark-Houwink-Sakurada relation (Equation 7), the value of intrinsic viscosity changes with the molecular mass of the polymer as:

$$[\eta] = K\,M^{a} \qquad \textbf{(7)}$$

where the two parameters *K* and *a* are related to the "stiffness" of the chain and depend on the type of polymer, solvent and temperature [14,15].

The aim of this work was to obtain viscometric parameters (intrinsic viscosity and constants values) of cyclohexane solutions of high-*cis* polybutadienes by graphic extrapolation and by a single point determination. The viscosity-average molecular mass, determined employing the values of intrinsic viscosity obtained by the six different equations, were compared. It is remarkable the fact that the determination of viscometric parameters by a faster method, as single point determination, is important especially in industry laboratories. In this way, percentual differences of the values of intrinsic viscosity obtained by graphic extrapolation (Equations 1, 2, 3 and 4) and a single point determination (Equations 4, 5 and 6) were compared as well as the percentual differences values of molecular mass obtained by both methods. The validity of the single point determination for high-cis-polybutadiene, in the conditions analyzed, was evaluated.

Experimental

Five different samples of high-*cis* polybutadiene were used in this study: BR-1, BR-2, BR-3, BR-4 and BR-5. These samples were prepared using a catalyst system based on neodymium, according to the procedure described in literature [16].

Number-average and weight-average molecular masses were determined by size exclusion chromatography (SEC), in a Waters 150-C Plus apparatus, fitted with a RI detector, at 30ºC, using THF as solvent, at 1mL/min flow rate. Monodisperse polystyrene standards were employed to obtain the calibration curve.

Viscometric parameters determinations were carried out at 30 ± 0.1°C, in concentration values of 0.25 or 0.125% (w/v) of cyclohexane solutions, (dependinng on the molecular mass), using an Ubbelohde 0B viscosimeter. By graphic extrapolation to infinite dilution, experimental determination was carried out by counting the efflux time of six dilutions of the samples solutions. In single point determination, the lowest value of dilution was chosen for the calculations. At low polymer concentrations the formation of entanglements among the macromolecules is minimized. That condition assures that all determinations are performed in newtonian flow. For viscosity-average molecular mass ($\overline{M}v$) determination the constants $K = 11.2 \times 10^3$ mL/g and $a = 0.75$ were employed [17].

Results and discussion

Table 1 shows the primary experimental data for all samples. Figure 1 presents the relation between log η_{sp} and log c[η] obtained for the samples analyzed. The linear relations indicated that all determinations were performed in newtonian flow.

Table 1. The primary experimental data for all samples

BR-1	C (g/dL)	η_r (dL/g)	η_{sp} (dL/g)	η_{red} (dL/g)	η_{inh} (dL/g)
Mother-sol	0.130	1.388	0.388	2.984	2.521
Dilution 1	0.108	1.320	0.320	2.954	2.563
Dilution 2	0.093	1.272	0.272	2.928	2.590
Dilution 3	0.081	1.237	0.237	2.915	2.616
Dilution 4	0.072	1.211	0.211	2.915	2.645
Dilution 5	0.065	1.188	0.188	2.894	2.652
BR-2	C (g/dL)	η_r (dL/g)	η_{sp} (dL/g)	η_{red} (dL/g)	η_{inh} (dL/g)
Mother-sol	0.285	1.785	0.785	2.755	2.033
Dilution 1	0.238	1.639	0.639	2.690	2.080
Dilution 2	0.204	1.539	0.539	2.646	2.117
Dilution 3	0.178	1.462	0.462	2.592	2.131
Dilution 4	0.158	1.406	0.406	2.564	2.152
Dilution 5	0.143	1.362	0.362	2.543	2.170
BR-3	C (g/dL)	η_r (dL/g)	η_{sp} (dL/g)	η_{red} (dL/g)	η_{inh} (dL/g)
Mother-sol	0.425	2.042	1.042	2.451	1.680
Dilution 1	0.354	1.833	0.833	2.353	1.712
Dilution 2	0.304	1.693	0.693	2.282	1.734
Dilution 3	0.266	1.597	0.597	2.249	1.763
Dilution 4	0.236	1.524	0.524	2.219	1.784
Dilution 5	0.213	1.466	0.466	2.195	1.801
BR-4	C (g/dL)	η_r (dL/g)	η_{sp} (dL/g)	η_{red} (dL/g)	η_{inh} (dL/g)
Mother-sol	0.260	1.405	0.405	1.558	1.308
Dilution 1	0.217	1.336	0.336	1.548	1.335
Dilution 2	0.186	1.282	0.282	1.521	1.340
Dilution 3	0.163	1.246	0.246	1.512	1.352
Dilution 4	0.144	1.216	0.216	1.493	1.352
BR-5	C (g/dL)	η_r (dL/g)	η_{sp} (dL/g)	η_{red} (dL/g)	η_{inh} (dL/g)
Mother-sol	0.270	1.373	0.373	1.381	1.174
Dilution 1	0.225	1.308	0.308	1.368	1.193
Dilution 2	0.193	1.261	0.261	1.353	1.202
Dilution 3	0.169	1.225	0.225	1.336	1.205
Dilution 4	0.150	1.199	0.199	1.328	1.211
Dilution 5	0.135	1.178	0.178	1.321	1.216

C = concentration; η_r = relative viscosity; η_{sp} = specific viscosity; η_{red} = reduced viscosity; η_{inh} = inherent viscosity; efflux time of the solvent: t_0 = 236.51s.

Viscosimetric data, obtained by graphic extrapolation, were determined employing Equations 1 to 4. Figure 2 shows linear relations obtained by Huggins (H) equation for all samples. The same graphic profile was verified when Kraemer (K), Martin (M) and Schulz-Blaschke (SB) equations were concerned. Table 2 presents the intrinsic viscosity values calculated from all equations and Table 3 shows the viscometric constants obtained for all samples of high-*cis* polybutadiene analyzed in this work. In Table 4, the percentual differences ($\Delta\%$) obtained for intrinsic viscosity values calculated by graphic extrapolation, by K, M and SB equations, and by the single point method, by SB, Solomon-Ciuta (SC) and Deb-Chantterjee (DC) equations, taking H intrinsic viscosity, $[\eta]_h$, as a reference.

Table 2 shows that the values of intrinsic viscosity calculated by both methods are very close which can be confirmed by the low percentual differences values observed in Table 4, which varied in the range from -2.92 to 2.74 %. Single-point determinations were carried out using the point at the lowest polymer concentration. However, if the highest value of polymer concentration (0.425 g/dL) is used, the single-point determination still shows adequate results ($[\eta]_{sc}$ = 1.906 dL/g ; $[\eta]_{dc}$ = 2.032 dL/g and $[\eta]_{sb}$ = 1.897 dL/g).

Table 3 shows that, for all samples analyzed, $k_h < 0.5$, hence cyclohexane should be considered a good solvent for high-*cis* polybutadiene, based on experimental reports that indicate that values lower than 0.5 are obtained for diluted polymer solutions in good solvents. That conclusion is supported by k_k since negative values of Kraemer coefficients indicate good polymer solvation [11,18].

Solomon-Ciuta (SC) and Deb-Chantterjee (DC) equations are based on the premises of the relation $k_h + k_k = 0.5$ [9]. Therefore, their application should be restricted to Huggins and Kraemer constants values. Table 3 shows that none of the constant results fitted the relation. However, the low percentual differences values of intrinsic viscosity obtained when those two equations were compared to Huggins, suggest no restriction for the application of SC and DC equations for this system.

Schulz-Blaschke constant, k_{sb}, values obtained for the samples by graphic extrapolation, varying in the range from 0.15 to 0.25 (Table 3), were different from 0.28, which is commonly employed in single point determinations for many polymer systems [10,11]. Nevertheless, the use of the latter value in single point determination produced $[\eta]_{sb}$ values very close to those obtained by extrapolation (Table 2). It is remarkable that the percentual differences obtained for intrinsic viscosity values from SB equation by a single point determination, employing $k_{sb} = 0.28$, were lower than those calculated by graphic extrapolation, which were expected to be a more precise determination. That is an indication that $k_{sb} = 0.28$ is suitable for high-*cis*-polybutadiene in cyclohexane, at 30°C.

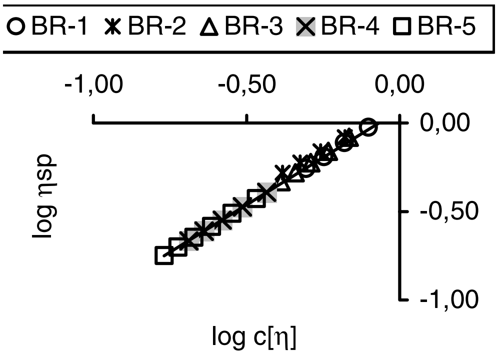

Figure 1. Log η_{sp} *versus* log c[η] for all samples

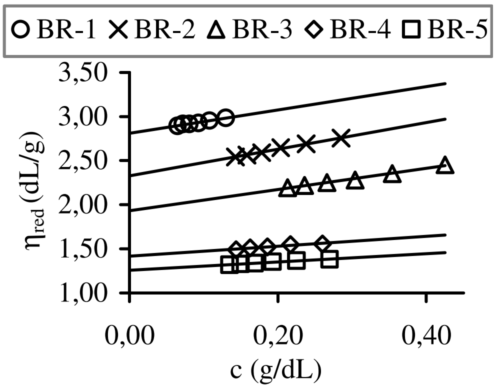

Figure 2. Huggins viscosity for all samples

Table 2. Intrinsic viscosity values determined for high-*cis* polybutadiene in cyclohexane, at 30°C

Sample	$[\eta]_h$ [a] (dL/g)	$[\eta]_k$ [a] (dL/g)	$[\eta]_m$ [a] (dL/g)	$[\eta]_{sb}$ [a] (dL/g)	$[\eta]_{sb}$ [b] (dL/g)	$[\eta]_{sc}$ [c] (dL/g)	$[\eta]_{dc}$ [c] (dL/g)
BR-1	2.811	2.787	2.816	2.816	2.749	2.729	2.769
BR-2	2.327	2.303	2.344	2.360	2.309	2.286	2.355
BR-3	1.931	1.917	1.959	1.984	1.942	1.923	1.983
BR-4	1.417	1.411	1.421	1.424	1.408	1.403	1.427
BR-5	1.260	1.256	1.263	1.266	1.258	1.248	1.265

[a] Calculated by graphic extrapolation.
[b] Calculated through a single point determination (k_{sb} = 0.28).
[c] Calculated through a single point determination.

Table 3. Viscometric constants calculated for high-*cis* polybutadiene

Sample	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
BR-1	0.166	-0.408	0.156	0.153	-0.242
BR-2	0.281	-0.177	0.244	0.217	0.104
BR-3	0.322	-0.155	0.266	0.224	0.167
BR-4	0.281	-0.191	0.258	0.242	0.090
BR-5	0.292	-0.187	0.268	0.253	0.105

Table 4. Percentual differences (Δ%) obtained for intrinsic viscosity values calculated by graphic extrapolation (Kraemer (K), Martin (M) and Schulz-Blaschke (SB) equations) and by a single point measurement (Schulz-Blaschke (SB), Solomon-Ciuta (SC) and Deb-Chantterjee (DC) equations), taking Huggins intrinsic viscosity, $[\eta]_h$, as a reference

Sample	Percentual differences (Δ%)[a] for intrinsic viscosity values					
	Graphic extrapolation			Single point determination		
	K	M	SB	SB	SC	DC
BR-1	-0.85	0.18	0.18	-2.21	-2.92	-1.49
BR-2	-1.03	0.73	1.42	-0.77	-1.76	1.20
BR-3	-0.73	1.45	2.74	0.57	-0.41	2.69
BR-4	-0.42	0.28	0.49	-0.64	-0.99	0.71
BR-5	-0.32	0.24	0.48	-0.16	-0.95	0.40

[a] $\Delta\,\% = [100\,([\eta]\,/\,[\eta]_h)] - 100$

By comparing (SB), Solomon-Ciuta (SC) and Deb-Chantterjee (DC) equations used in the single point determination, it is notable the fact that intrinsic viscosity values obtained from DC equation produced the smallest percentual differences when compared with those obtained from Huggins equation, by graphic extrapolation. These results indicate that, for the systems analyzed in this work, Deb-Chantterjee equation seems to be the best.

Table 5. Intrinsic viscosity of Huggins $[\eta]_h$ and molecular mass values of high-*cis* polybutadiene obtained by SEC and viscosimetry

Sample	$[\eta]_h$	Molecular Mass (x 10^{-5})								
		$\overline{M}n$[a]	$\overline{M}w$[a]	$\overline{M}v_h$	$\overline{M}v_k$	$\overline{M}v_m$	$\overline{M}v_{sb}$	$\overline{M}v_{sb}$[b]	$\overline{M}v_{sc}$	$\overline{M}v_{dc}$
BR-1	2.811	1.03	4.11	7.35	7.26	7.36	7.36	7.13	7.06	7.20
BR-2	2.327	0.93	3.40	5.72	5.64	5.77	5.82	5.66	5.58	5.81
BR-3	1.931	0.57	2.89	4.45	4.41	4.54	4.62	4.49	4.43	4.61
BR-4	1.417	0.48	2.25	2.95	2.93	2.96	2.97	2.92	2.91	2.97
BR-5	1.260	0.44	2.23	2.52	2.51	2.53	2.54	2.52	2.49	2.54

[a] SEC - THF at 30°C; [b] $k_{sb} = 0.28$

Table 5 shows a concomitant reduction in intrinsic viscosity and molecular mass values, as expected. It also presents a comparison between molecular mass values of high-*cis* polybutadienes obtained by size exclusion chromatography (SEC) [16] and by viscometry, employing intrinsic viscosity values obtained by using Equations 1-6. By comparing the two techniques, differences in the values are evident. The discrepancy is probably due to the diversification in analysis conditions, as differences in: techniques, standards employed and solvents. Among the viscosity-average molecular mass values obtained by a single point determination, the three equations employed (SB, SC and DC) showed results not much different from those obtained by graphic extrapolation.

The percentual differences (Δ%) obtained for viscosity-average molecular mass values are showed in Table 6. These values were calculated taking $\overline{M}v$ determined by Huggins equation as a reference. Among the molecular mass values obtained by a single point determination, the three equations employed (SB, SC and DC) showed results close to those obtained by graphic extrapolation. Moreover, it was observed a tendency of decreasing in the values of Δ% as the molecular masses decrease. Deb-Chantterjee equation presented the smallest percentual differences, being more suitable to be applied in the faster determination of molecular mass for the system high-*cis*-polybutadiene in cyclohexane, at 30° C.

Table 6. Percentual differences (Δ%) obtained for viscosity-average molecular mass values

Sample	Percentual difference (Δ%)[a]					
	$\overline{M}v_{sb}$	$\overline{M}v_{k}$	$\overline{M}v_{m}$	$\overline{M}v_{sc}$	$\overline{M}v_{dc}$	$\overline{M}v_{sb}$[b]
BR-1	0.14	-1.22	0.14	-3.95	-2.04	-2.99
BR-2	1.75	-1.40	0.87	-2.45	1.57	-1.05
BR-3	3.82	-0.90	2.02	-0.45	3.60	0.90
BR-4	0.68	-0.68	0.34	-1.34	0.68	-1.02
BR-5	0.79	-0.40	0.40	-1.19	0.79	0.00

[a] $\Delta\,\% = [100\,([\eta]\,/\,[\eta]_h)] - 100$

[b] $K_{sb} = 0.28$

Conclusions

Viscometric parameters determined by graphic extrapolation and by a single point determination were in good accordance, being the latter type of calculation, which is much more rapid, suitable for the high-*cis* polybutadiene in cyclohexane; at 30°C. That way, intrinsic viscosity values and specially viscosity-average molecular mass results should be calculated by the determination of the efflux time of only one concentration of polymer solution. The accuracy of this method is especially important for quality control laboratories. Deb-Chantterjee equation, which is independent of any predetermined constant value, produced lower percentual differences when compared with Schulz-Blaschke and Solomon-Ciuta equations, showing to be more accurate for the calculations. Schulz-Blaschke constant value (0.28), employed for many polymer systems in single point determinations, were also suitable for being applied in the system analyzed in this work. It was verified that, for all the samples, Huggins constants were lower than 0.5 indicating that cyclohexane is a good solvent for high-*cis* polybutadiene, at 30°C. This result was confirmed by negative Kraemer constant which also indicates good solvation.

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