

In-line monitoring of weight average molecular weight in solution polymerizations using intrinsic viscosity measurements

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Abstract

The main objective of this work is developing a simple viscometrical method for in-line monitoring and control of weight average molecular weight (\bar{M}_w) in solution polymerizations. The method is based on the evaluation of the approximate intrinsic viscosity of the polymer solution, at each sampling time, using a single measurement of the flow time of a diluted polymer solution through a capillary tube. Experiments were carried out for peroxide initiated styrene solution polymerization reactions in a tubular reactor. Results obtained for approximate intrinsic viscosities are in agreement with the intrinsic viscosity values published in the literature and allow fast and fair in-line values for \bar{M}_w . © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Intrinsic viscosity; Capillary viscometer; In-line weight average molecular weight

1. Introduction

The nonlinear behavior of polymerization systems and the difficulties of sensor development, which requires knowledge and understanding of process, reactor design, mathematical modeling, control techniques, instrumentation and multi-disciplinary fields, make sensor technology a difficult task. This is why in-line monitoring of polymer properties is complex in nature, in spite of the efforts to develop density, viscosity, surface tension, refractive index, composition, light scattering and chromatographic methods for the evaluation of polymer characteristics [1,2].

There is much interest in the in-line monitoring and control of molecular weight distributions (MWD) during polymerization reactions as this may be regarded to be among the most important molecular properties of polymer resins. However, the analysis of polymer chain length using gel permeation chromatography (GPC), size exclusion chromatography (SEC), and light scattering, requires very expensive, sophisticated, time-consuming and unreliable (at industrial environments) instruments. From a practical point of view, most of the times, the whole MWD is not needed and significant amount of information about the end-use properties of the polymer resins may be provided by the leading moments of the MWD, such as the weight average

molecular weight (\bar{M}_w) [3]. Even in this case, however, techniques for in-line monitoring of \bar{M}_w are not well developed [1,2].

In-line viscometers are useful for monitoring the evolution of polymerization reactions and are widely used as an indirect measurement of the average molecular weight of polymer solutions [1,2,4–6]. However, as the individual effects of conversion and molecular weight on viscosity are not readily separable, it is very difficult to use viscosity techniques at middle and high conversions [1,2]. In principle, the intrinsic viscosity $[\eta]$ of a polymer solution does not depend on conversion and may be very useful for in-line monitoring of average molecular weight of polymer resins. In spite of the huge amount of information available about $[\eta]$ in the literature, attempts to monitor $[\eta]$ in-line and use this value to predict the average molecular weight of the polymer resin have not been made.

By measuring the intrinsic viscosity of polymer solutions, the polymer average molecular weight can be predicted through the Mark–Houwink empirical equation, as described by

$$[\eta] = K\bar{M}_v^a \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, K and a are the parameters that depend on the solvent/polymer pair and \bar{M}_v the viscosity–average molecular weight of the polymer. If the shape of the molecular weight distribution does not change significantly, as usually observed in continuous free-radical

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solution polymerizations, then \bar{M}_v usually is a multiple of \bar{M}_w , so that \bar{M}_v can be normally replaced by \bar{M}_w in Eq. (1) [7,8].

The intrinsic viscosity can be determined experimentally through measurements of the specific viscosity, defined in the following equation

$$\eta_{sp} = \frac{t - t_0}{t_0} \quad (2)$$

where η_{sp} is the specific viscosity, t the flow time of a polymer solution through a capillary tube of known diameter and length and t_0 the flow time of the pure solvent through the same capillary tube.

The intrinsic viscosity is described as the limit of the ratio between the specific viscosity (η_{sp}) and the polymer concentration (c), as the polymer concentration approaches zero,

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (3)$$

Experimentally, the specific viscosity is measured for at least three different polymer concentrations and a plot of (η_{sp}/c) versus c is extrapolated for zero concentration, leading to high precision intrinsic viscosity measurements. However, this method is not appropriate for in-line monitoring of \bar{M}_w because of the large lag-time required. Besides, it is difficult to precisely control the polymer concentration of very diluted solutions at plant site.

In the literature one may find faster methods for obtaining the intrinsic viscosity based on a single point determination of the specific viscosity. Kraemer [9] and Huggins [10] were the first to propose empirical equations for describing how the intrinsic viscosity varies with the polymer solution concentration, Eqs. (4)–(6). Therefore, assuming that the polymer concentration c is known, it is possible to evaluate $[\eta]$ based on a single measurement of the specific (relative) viscosity. In both cases, however, it is necessary to know an additional parameter (k_1 and k_2) that is usually unavailable. Besides, these additional parameters may depend on the polymer characteristics and on the polymer/solvent pair, which means that they have to be estimated simultaneously with $[\eta]$. Therefore, in practice three or more values of the specific (relative) viscosity for different polymer concentrations are required for evaluation of $[\eta]$ with Eqs. (4)–(6) [11], unless additional assumptions are introduced into the problem formulation.

$$\frac{\eta_{sp}}{c} = [\eta] + k_1[\eta]^2c \quad (4)$$

$$\ln \frac{\eta_{rel}}{c} = [\eta] + k_2[\eta]^2c \quad (5)$$

$$\eta_{rel} = \frac{t}{t_0} \quad (6)$$

Gomes and coworkers [11] showed, however, that quadratic approximations of the function that relates the specific viscosity of polymer solutions with the polymer concentration

may lead to values of intrinsic viscosity that are much more uncertain than the values obtained through simpler linear fits. Schultz and Blaschke [12] developed an alternative first-order approximation, as shown in Eq. (7), that also depends on an additional model parameter k . Solomon and Ciuta [13] obtained an equation that may lead to the intrinsic viscosity value with a single point viscosity measurement and that does not depend on any additional parameter describing the solvent–polymer characteristics, Eq. (8). Baruah and Laskar [14] determined the parameters of the Mark–Houwink equation for the polydispersed poly(*n*-docosylacrylate) solutions of 0.5% w/v, using intrinsic viscosity data calculated by the single point method described by Solomon and Ciuta [13]. It was observed that Eq. (8) yielded accurate intrinsic viscosities and high reproducibility when measurements were made for dilute polymer solutions, with concentrations below 0.2% w/v. However, such low concentrations are inadequate for most practical industrial applications.

$$[\eta] = \frac{\eta_{sp}}{[c(1 + k\eta_{sp})]} \quad (7)$$

$$[\eta] = \frac{\sqrt{2}}{c} \sqrt{\eta_{sp} - \ln \eta_{rel}} \quad (8)$$

2. Intrinsic viscosity determination

For in-line monitoring and control of \bar{M}_w , η_{sp} is assumed here to be a simple linear function of the polymer concentration (c), as shown in Eq. (9). The linear coefficient, the approximate intrinsic viscosity $[\eta^{ap}]$, is assumed here to follow the Mark–Houwink empirical equation, Eq. (10). This may provide a simple and fast procedure for monitoring of \bar{M}_w , requiring the preparation of a single sample of the polymer solution. Therefore, a single concentration-viscosity measurement must be performed for a dilute polymer solution in a capillary viscometer at a fixed temperature, yielding real-time \bar{M}_w information obtained from a Mark–Houwink calibration.

$$[\eta^{ap}] = \frac{t - t_0}{t_0} \frac{1}{c} \quad (9)$$

$$[\eta^{ap}] = KM_w^a \quad (10)$$

η_{sp} may be measured experimentally with numerous commercial in-line capillary viscometers available in the market. Viscotek provides the Semi Automated Sample Preparation (SASP), which comprises a balance, a syringe pump and a computer [15]. From Viscologic, the instrument named Visiologic runs automatically all the operations of dilution, stirring, cleaning, draining and sequential measurements of flows [16]. Lauda commercializes the PVS viscometry measuring system with a program-controlled burette for solvent addition, automatic cleaning and flow-time

measurement of viscosities at different concentrations. Parallel operation permits a sample throughput of eight samples per hour [17]. Besides, Fig. 1 shows how the specific viscosity depends on the polymer solution concentrations for typical polystyrene/solvent systems. It may be observed that the linear behavior is approximately valid up to polymer concentrations around 1.0 g/dl.

In order to validate the strategy presented here, the peroxide initiated solution styrene polymerization reaction is carried out in a 12-m long tubular reactor. The feed solution contains a 40–60 w/w% monomer–solvent solution and 0.05 kmol/m³ initiator concentration. Description of the experimental unit can be found elsewhere [18]. A digital densitometer, Anton Paar mPDS-2000, is used to monitor monomer conversion in-line. Samples of the polystyrene solutions were withdrawn every 1800 s for dilution and feeding into a capillary viscometer. Diluted solutions were prepared at room temperature by diluting the original

mer solutions were measured with a Cannon–Ostwald–Fenski capillary viscometer at a temperature of 30 ± 0.1°C maintained with a thermostatic controlled bath (Haake). The viscometer was selected in order to lead to a flow time above 100 s. The lag-time between sampling and viscosity measurements includes dilution and homogenizing (100 s), flow-time measurements (up to 600 s) and cleaning procedures (100 s). No attempt was made to minimize the lag-time in this work, but some operation parameters may be used to minimize the measurement time, such as the diameter of the feeder and mixer tubing, the overall flow rates and the amount of reaction solution sampled. Polymer samples, prepared at different reaction conditions, were also characterized through SEC measurements carried out in solutions of tetrahydrofuran (THF). \bar{M}_w (obtained from SEC measurements) and viscosity data were used in order to build a Mark–Houwink empirical equation for estimating polymer quality in-line.

$$c = \frac{100 \times X}{X/d_p + (1 - X)/d_s + M_{T0}/M_{S0} \times 1/d_T + \frac{V_{ADD}}{V_{OUTLET} \left(\frac{1}{d_s} + \frac{M_{T0}}{M_{S0}} \times \frac{1}{d_T} \right)}} \quad (11)$$

sample with pure toluene in order to reach a final polymer concentration in the range from 0.1 to 0.5 g/dl. No sort of purification of the final polymer solutions was performed. The polymer concentration (c) was calculated as shown in Eq. (11) with the help of the process densitometer, which provides in-line monomer conversion (X) data of the tubular reactor outlet stream. Remaining variables are the measured volumes of the reactor sample (V_{OUTLET}) and of the pure toluene employed for dilution (V_{ADD}), initial toluene and styrene mass concentrations of the feeding tank (M_{T0} , M_{S0} , respectively) and polystyrene (d_p), styrene (d_s) and toluene (d_T) density values. The rheological properties of the poly-

3. Results and discussion

Three runs named A, B and C were carried out in the tubular reactor. During 4 h, the system operation conditions (temperature, flow, feed concentration) were unchanged for reaction A. After this period, a step perturbation of the feed modifier concentration was implemented. The tert-dodecylmercaptan (TDM) feed concentration was varied from zero to 0.001 kmol/m³, keeping the reactor temperature at 79°C through out the experiment. In reaction B, after attaining steady-state conditions, simultaneous step perturbations of the temperature and TDM concentration were implemented, from 65 to 80°C and from zero to 0.0004 kmol/m³, respectively. Reaction C was similar to reaction B, but serial step temperature perturbations from 50 to 92°C and a TDM concentration step perturbation from zero to 0.05 kmol/m³ were performed. Samples were withdrawn every sampling time from the outlet stream of the tubular reactor, containing polystyrene, unreacted monomer, modifier, initiator and solvent, and were diluted using toluene for introduction in to the capillary viscometer.

Table 1 illustrates the small intrinsic viscosity differences [$\Delta\eta$] obtained when Eqs. (8) and (9) are compared for the diluted samples of reactions A, B and C.

Fig. 2 presents results obtained with solutions prepared with the pure and dry polymer samples and with the original diluted reactor samples. The pure polymer sample comprises toluene and styrene with the same proportion as the original diluted reactor sample, but with purified (dry)

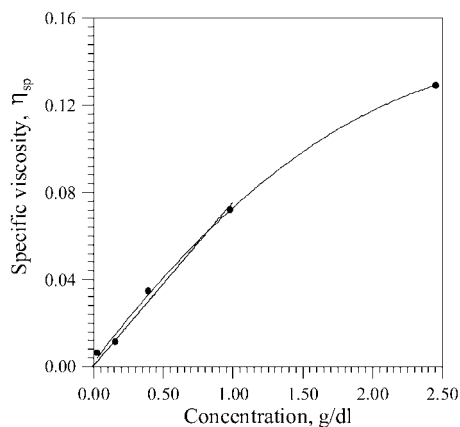


Fig. 1. Specific viscosities as a function of polymer concentration for typical polystyrene/toluene solutions.

Table 1
Experimental η_{sp} and \bar{M}_w data

Reaction	$[\eta]$, [13] (dl/g)	c (g/dl)	$[\eta^{ap}]$, Eq. (9) (dl/g)	$\Delta\eta$ (dl/g)	\bar{M}_w , SEC measurements (g/gmol)	
A	0.12	0.2785	0.12	0.00	17 840	
	0.15	0.2896	0.15	0.00	18 740	
	0.14	0.3112	0.15	0.01	17 412	
	0.14	0.2868	0.14	0.00	18 054	
	0.15	0.2604	0.15	0.00	17 833	
	0.14	0.3080	0.14	0.00	18 555	
	0.14	0.2764	0.14	0.00	17 540	
	0.14	0.2888	0.14	0.00	17 366	
	0.13	0.2992	0.13	0.00	16 375	
	0.14	0.3472	0.14	0.00	18 268	
	0.14	0.3184	0.14	0.00	16 922	
	0.15	0.3232	0.15	0.00	17 490	
	0.15	0.2660	0.15	0.00	16 925	
	0.14	0.2916	0.14	0.00	16 591	
	0.15	0.3416	0.15	0.00	18 140	
	0.14	0.3420	0.14	0.00	16 774	
	0.13	0.3052	0.14	0.01	17 464	
	0.14	0.2884	0.14	0.00	17 453	
	0.12	0.2956	0.13	0.01	15 781	
	0.12	0.2900	0.12	0.00	15 732	
	0.13	0.3188	0.13	0.00	16 116	
	B	0.23	0.2933	0.24	0.01	29 094
		0.23	0.2600	0.23	0.00	28 955
0.20		0.2860	0.20	0.00	23 140	
0.19		0.3044	0.19	0.00	22 007	
0.18		0.3016	0.19	0.01	21 088	
0.18		0.2776	0.18	0.00	20 646	
0.17		0.2880	0.18	0.01	19 605	
0.16		0.2828	0.16	0.00	20 556	
0.17		0.3076	0.17	0.00	20 363	
0.17		0.274	0.18	0.01	20 815	
0.17		0.3228	0.17	0.00	19 556	
0.18		0.3092	0.18	0.00	19 777	
0.18		0.3196	0.19	0.01	22 035	
0.16		0.3032	0.17	0.01	22 195	
0.15		0.3072	0.15	0.00	18 926	
0.14		0.3164	0.14	0.00	15 620	
0.14		0.3020	0.14	0.00	12 313	
0.13		0.3044	0.13	0.00	12 245	
0.13		0.3068	0.13	0.00	12 763	
0.14		0.2904	0.14	0.00	12 961	
0.13		0.2924	0.13	0.00	12 968	
0.13		0.3024	0.13	0.00	13 059	
0.13		0.2804	0.14	0.01	12 925	
C	0.49	0.2732	0.51	0.02	146 574	
	0.35	0.2748	0.36	0.01	96 172	
	0.30	0.2544	0.31	0.01	76 518	
	0.29	0.2608	0.30	0.01	65 877	
	0.26	0.2528	0.27	0.01	62 763	
	0.25	0.2412	0.26	0.01	53 980	
	0.24	0.2832	0.24	0.00	49 149	
	0.23	0.2632	0.24	0.01	47 078	
	0.22	0.2544	0.23	0.01	44 514	
	0.22	0.2636	0.22	0.00	39 559	
	0.20	0.2496	0.20	0.00	37 565	

Table 1 (continued)

Reaction	$[\eta]$, [13] (dl/g)	c (g/dl)	$[\eta^{ap}]$, Eq. (9) (dl/g)	$\Delta\eta$ (dl/g)	\bar{M}_w , SEC measurements (g/gmol)
C	0.12	0.2432	0.12	0.00	18 097
	0.07	0.2444	0.07	0.00	7968
	0.07	0.2420	0.07	0.00	5522
	0.08	0.2476	0.08	0.00	4635
	0.06	0.2620	0.06	0.00	3993
	0.06	0.2472	0.06	0.00	4110
	0.06	0.1368	0.06	0.00	4501
	0.06	0.2392	0.06	0.00	4225
	0.07	0.2432	0.07	0.00	3896
	0.06	0.2472	0.06	0.00	4162
	0.06	0.3076	0.06	0.00	4309
	0.05	0.2580	0.05	0.00	4203
	0.05	0.2556	0.05	0.00	4156
	0.05	0.2480	0.05	0.00	4140
0.06	0.2696	0.06	0.00	4388	

polystyrene. It can be observed that results are almost the same. Therefore, the proposed viscometrical method does not require the tedious and time-consuming sampling of the reaction mixture, followed by separation, washing and drying of the polymer product, steps which have been frequently employed, prohibiting in-line application of the method.

Table 2 shows results for two polystyrene samples with very different \bar{M}_w . It can be observed that the accuracy of the viscometer is about 0.01 dl/g.

Differentiating Eq. (12) with respect to polymer concentration (Eqs. (13) and (14)) and the Mark–Houwink Equation (Eq. (15)) with respect to \bar{M}_w (Eqs. (16)–(18)), it can be observed that the relative error of the intrinsic viscosity is of the same order of magnitude of the relative error of the concentration detector, but that the relative error of the \bar{M}_w is larger than the relative error of the polymer concentration, as a is smaller than 1. Therefore, good accuracy is required for polymer concentration measurements.

$$[\eta^{ap}] = \frac{\eta_{sp}}{c} \quad (12)$$

$$\Delta[\eta^{ap}] = -\left(\frac{\eta_{sp}}{c^2}\right)\Delta c \quad (13)$$

$$\frac{\Delta[\eta^{ap}]}{[\eta^{ap}]} = -\frac{\Delta c}{c} \quad (14)$$

$$[\eta^{ap}] = KM_w^a \quad (15)$$

$$\Delta[\eta^{ap}] = aKM_w^a \frac{\Delta M_w}{M_w} \quad (16)$$

$$\frac{\Delta[\eta^{ap}]}{[\eta^{ap}]} = a \frac{\Delta M_w}{M_w} \quad (17)$$

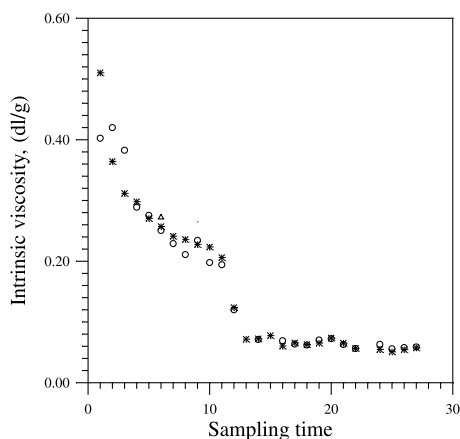


Fig. 2. Intrinsic viscosities of polystyrene samples in reaction C measured rigorously from dry (*) and pure (Δ) polymer and approximately from the original reactor samples (○).

$$\frac{\Delta M_w}{M_w} = -\frac{1}{a} \frac{\Delta c}{c} \quad (18)$$

\bar{M}_w of polymer samples isolated from reactions A, B, and C were determined by SEC, as can be seen in Fig. 3. These data were used for estimating the parameters of the Mark–Houwink equation, using intrinsic viscosity information from Table 1. Eq. (19), for polystyrene in toluene, is the equation obtained between η^{ap} and \bar{M}_w when a quasi-Newton non-linear regression method is used [19]. The parameters of the Mark–Houwink equation for polystyrene in solution of toluene at 30°C were estimated using \bar{M}_w values ranging from 3800 to 150 000 g/gmol. Results may be regarded as excellent and adequate for control purposes. \bar{M}_w values estimated with Eq. (19) are almost always within the error bounds of the SEC method, even when uncertainties of the η_{sp} measuring technique are neglected. Fig. 3 shows very clearly that \bar{M}_w evaluation may be based upon single measurements of η_{sp} , from samples collected directly from the reactor, without any further purification.

$$[\eta^{ap}] = 68.7 \times 10^{-5} M_w^{0.55}, \text{ in dl/g} \quad (19)$$

According to data provided by Brandrup and Immergut [20], the intrinsic viscosity of polystyrene in solutions of toluene

Table 2
Accuracy of the measurements

c (g/dl)	$[\eta^{ap}]$ (dl/g)	$[\bar{\eta}^{ap}]$ (dl/g)	$\Delta[\eta^{ap}]$ (dl/g)	Repeatability (dl/g)
0.3987	0.11		0.00	
	0.12		-0.01	
	0.12	0.11	-0.01	0.01
	0.10		0.01	
	0.11		0.00	
0.4926	1.04		0.02	
	1.07		-0.01	
	1.06	1.06	0.00	0.02
	1.06		0.00	
	1.07		-0.01	

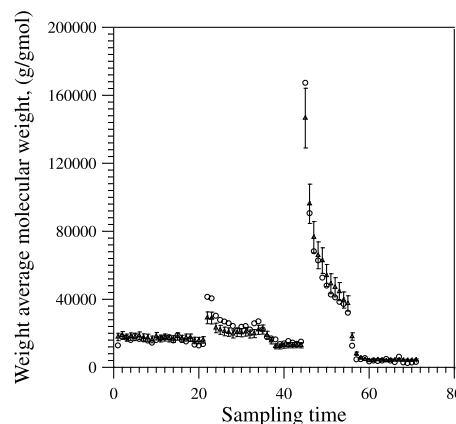


Fig. 3. Chain length obtained both from SEC (Δ) and in-line intrinsic viscosity measurements (○).

at 30°C is given by Eq. (20). Although Eq. (20) seems to be very different from Eq. (19), Fig. 4 shows that Eqs. (19) and (20) actually lead to very similar values of the intrinsic viscosity, which means that Eq. (19) provides very good estimates of $[\eta]$ in the range analyzed, in spite of the simplifications and simplicity of the single point method. Actually, as shown by Gomes [11], it is very difficult to estimate K and a independently in Eq. (10), given the huge correlation between these two parameters. This is why Eqs. (19) and (20) lead to very similar results of $[\eta]$ in spite of the different parameter sets considered. For most practical reasons, though, Figs. 3 and 4 show that the single point method presented here may be used with confidence for in-line monitoring and control of average molecular weights in solution polymerizations.

$$[\eta] = 11 \times 10^{-5} M_w^{0.71}, \text{ in dl/g.} \quad (20)$$

4. Conclusions

It is shown here that the in-line viscometrical method proposed allows the accurate monitoring of \bar{M}_w during the course of a solution polymerization reaction. The method depends on the sampling of the polymer solutions and on independent evaluations of monomer conversion. In spite of the fact that the concentration of the outlet stream changed during the reactions performed, the flow time of diluted polymer samples was dominated by the change in the chain length. Besides, the linear approximation for calculating intrinsic viscosity using a single concentration value of a reactor sample provided almost the same results provided by the single point relation method of Solomon and Ciuta [13].

The in-line viscometrical method was calibrated with the Mark–Houwink equation to allow real time evaluation of the weight average molecular weight. The simplicity of the method and short time required for analysis make this technique an extremely practical tool for monitoring and control of polymer quality in homogeneous reactions.

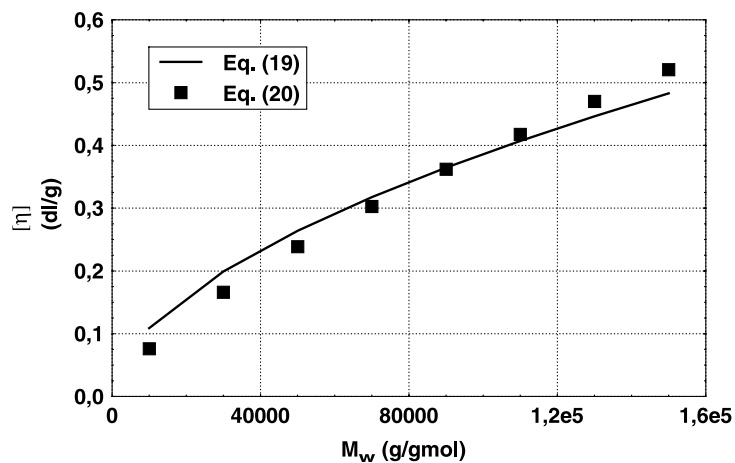


Fig. 4. Intrinsic viscosity of polystyrene in toluene solutions.

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