

Scaling equation for viscosity of polydimethylsiloxane in ethyl acetate: From dilute to concentrated solutions

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ABSTRACT

Rheology of polymer solutions suffers from lack of universal model of viscosity applicable across wide range of concentrations. Here we build such a model on the basis of measured viscosity of polydimethylsiloxane (PDMS) in ethyl acetate in a wide range of polymer concentrations: from dilute up to highly concentrated solutions. The relationship between viscosity and different polymer parameters in solution such as coil size, correlation length ξ , monomer–solvent and monomer–monomer interaction parameter were established experimentally as a function of concentrations [from 0.001 g/cm³ to 8.000 g/cm³], temperature [in a range 283–303 K] and molecular masses [9–139 kg/mol]. Entanglement onset at the crossover from dilute to semi-dilute solution as well as the solvent–monomer contact reduction at the crossover from semi-dilute to concentrated regime are captured by the model. This model is in accordance with the Eyring rate theory for activated processes.

1. Introduction

Processing of polymer materials in polymer/food industry requires precise control over flow of polymer solutions/ melts. Flow of polymer solutions is highly influenced by their intrinsic microstructure, which in turn is heavily dependent on the polymer molecular weight and its concentration [1,2]. Any changes in the nature of the flow can be quantitatively expressed through the viscosity of the solution. Therefore control of the process of polymer flow requires good understanding of viscosity of polymer solutions. The viscosity is dependent on monomer–solvent interactions (thus on chemical compositions), as well as some key length-scales of the system such as the hydrodynamic and gyration radii of the polymer coils (R_h and R_g respectively) and the correlation length ξ [3,4]. The correlation length strongly depends on concentration of polymer in solution. Therefore polymer solutions are usually classified into three characteristic categories depending on polymer concentration: dilute, semi-dilute and concentrated [2,5,6]. In a series of recent papers [3,7–9] we analysed the viscosity of polyethylene glycol (PEG) solutions in water in dilute and semi-dilute concentration regimes. We found a characteristic form of the viscosity for PEG–water solution [3,7,8]:

$$\eta = \eta_0 \exp \left[\left(\frac{\gamma}{RT} \right) \left(\frac{R_h}{\xi} \right)^a \right] \quad (1)$$

where η is the solution viscosity, η_0 is the solvent viscosity, R is the gas constant, T is temperature, a is a parameter of the order of unity and γ is an interaction parameter proportional to the activation energy of flow of the solution. This activation energy also depends on polymer concentration. Increasing concentration of polymers in solutions leads to reduction of polymer solvent contacts and thus changes the dominant interactions in the system from solvent–solvent and monomer–solvent interactions at dilute and semi-dilute solutions to monomer–monomer interactions in concentrated solutions [2,10–12]. In the present paper we validate Eq. (1) for a new system of polydimethylsiloxane in ethyl acetate; extend this equation to concentrated solutions and show the relation between the coil size and the polymer concentrations.

Different methods relating zero-shear viscosity to polymer concentration have been developed before, such as the ‘fuzzy-cylinder’ approach of Sato et al. [13]. There is a number of important parameters, necessary to characterize the viscosity across wide concentration range. The parameter ξ is defined as the correlation length of the system. For any entangled system, ξ is the average distance between the entanglement points of polymer chains [2,5,14] or in general it is a distance between the centre of masses of polymer coils. This correlation length is also named blob size (from de Gennes blob theory) or mesh size [2,5]. The correlation length is determined experimentally through

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light scattering techniques [4,7,8], and it depends on the concentration c as follows:

$$\xi = R_g \left(\frac{c}{c^*} \right)^{-\beta} \quad (2)$$

where, c^* is the concentration at the crossover from dilute to semi-dilute regime, β is a scaling exponent given by [2,15]:

$$\beta = -\nu(1 - 3\nu)^{-1} \quad (3)$$

The parameter ν is defined by the equation relating the radius of gyration to the molecular mass $R_g \sim M_w^\nu$. The value of ν is determined from the mean-field theory and is indicative of the repulsive excluded-volume interactions. As shown by Flory [16] in the mean field model, ν is 0.6 for polymers in good solvents. Therefore $\beta = 0.75$. The exponent a in Eq. (1) depends on the concentration regime and changes discontinuously at a crossover from dilute to semidilute regime. We found in PEG–water solutions [9] $a = \beta^{-1}$ for dilute regime and $a = R_h R_g^{-1} \beta^{-1}$ for semi-dilute regime of concentrations. In this paper we will determine this exponent also in the concentrated solutions of PDMS-ethyl acetate solution.

In dilute solutions polymer chains are far apart from each other and behave as isolated hard spheres [16]. Further subdivisions of the dilute regime at lower limits was postulated in theory [17–20], however with no practical implications since such concentrations essentially approach infinite dilution, and are not easily accessible through conventional experimental setups. The semi-dilute regime starts at concentrations such that polymer coils overlap. As the concentration increases the chains gradually interpenetrate each other and a uniform mesh-like structure is obtained [1,6]. This transition between separated coils (dilute regime) and interpenetrating coils (semi-dilute regime) occurs at a critical concentration c^* , where the coils simply touch each other [2, 5,14]:

$$c^* = \frac{M_w}{\frac{4}{3} \pi R_g^3 N_A} \quad (4)$$

where M_w is the molecular weight of the polymer, R_g is the radius of gyration, and N_A is the Avogadro number. From viscosity measurements Wisniewska et al. [1] observed that crossover between dilute and semi-dilute regime occurs at $R_h/\xi = 1$ i.e. at concentrations slightly different from c^* given by Eq. (4). There are other possible definitions of c^* , subject to assumptions of very specific packing arrangements of the sphere-like coils, as well as uncertainties in references for R_g which is usually measured at extremely dilute conditions [5,6,17]. Graessley et al. [21] further divided the semi-dilute region into two distinct subregimes: entangled and non-entangled [22]. Various properties of a polymer system such as its viscosity, elasticity [23] or fibre formation [24] is significantly influenced by the onset of entanglements. In this paper we assume classical division of polymer solutions into dilute, semi-dilute and concentrated regime.

Another parameter important for determining viscosity is the size of polymer coils in dilute, semi-dilute and concentrated solutions. As described by Cheng et al. [25], and Daoud et al. [6], coil dimensions start to decrease with increasing concentration of polymers. This is due to increased molar fraction of polymers in solution, reducing the number of solvent–monomer contacts. This regime of polymer solutions is named the concentrated regime, with the pure polymer melt being the extreme limit of this regime. Cheng et al. [25] presented an equation for the concentration at the onset of the transition between semi-dilute and concentrated regime:

$$c^{**} = \frac{R_g^{2(3\nu-1)/(2\nu-1)}}{R_g(\theta)} c^* \quad (5)$$

where $R_g(\theta)$ is R_g for the pure polymer melt [26]. The parameter $\nu = 0.6$ in the Flory model of polymer in good solvent [16]. However this model does not always conform to experimental data. Gagliardi et al. [27] determined in experiments that for linear polydimethylsiloxane chains,

the weighted average radius of gyration (in units of nanometre nm) is given by:

$$R_g = (0.0265 \pm 0.005) M_w^{0.53 \pm 0.02} \quad (6)$$

Thus in polydimethylsiloxane solutions $\nu = 0.53$ instead of 0.6.

In the past, various methods have been developed to predict the viscosity of polymer solutions for academic and industrial purposes [22, 28–30]. There have also been quite a few viscosity scaling paradigms defined, starting from the very basic well-known Martin equation [31]. However, previous approaches were valid in limited parameter space of concentrations (either in dilute regime, or semi-dilute or with-in some limits of these regimes), molecular masses and temperatures. One of the main problems with good model of viscosity is the lack of data such as: radius of gyration as a function of concentration and temperature for different polymer–solvent systems [6,25] or activation energy for flow at various thermodynamic conditions. Thus although thermodynamics of polymer solutions is well developed [32], the rheology of polymers is not.

In this paper we validate Eq. (1) against experimental data for PDMS-ethyl acetate solutions; extend this equation to concentrated solutions and find relation between the coil dimensions at higher concentrations. This polymer–solvent system has not been well studied in spite of the fact that both the polymer and the solvent individually are extremely common in various industrial and scientific applications [33–37]. We investigate the changes of the scaling parameters for such a system, through rheological measurements and literature data [1, 25,27,38]. Our approach opens a possibility to use viscosity data for full characterization of polymer–solvent system for industrial/scientific applications.

2. Materials and methods

Viscosity measurements at all temperatures and concentrations were performed using an Malvern Kinexus Pro Rheo-metre with a cone-plate and coaxial cylinder geometries. The dependence of viscosity on temperature was measured in the range of 283–303 K. Temperature was controlled within ± 0.1 K. Viscosity of dilute polymer solutions was close to the solvent viscosity. To provide more accurate data in this region, we performed experiments based on coaxial cylinder geometries. Polydimethylsiloxane (PDMS) of molecular weights 9, 28, 63, and 139 kg/mol were acquired from Alfa Aesar. Ethyl acetate was selected as the solvent for the PDMS system based on Hildebrand Solubility parameter values for good solvents [32,39] and procured in 99.2% pure form from Sigma Aldrich. We dissolved PDMS in ethyl acetate at 12 specific concentration ranging from 0.001 to 8.000 g/cm³. The solutions were allowed to stir at 800 rpm for 1–2 days and for highest molecular weight of PDMS for 3 days. The viscosity of these solutions were measured at temperatures intervals of 5 K. The measurements were performed on a Malvern Kinexus Pro Rheometer using cone-plate geometry. The geometry selected had an angular gradient of 0.02 radians. Shear rate was kept between 0.1–1000 s⁻¹ and the shear stress range was varied accordingly for the purpose of measurements. The linear viscosity data obtained were extrapolated to get the zero-shear viscosity. This zero-shear viscosity was then used as the viscosity of the polymer solution (see Table S1–S4, Fig S1 in supplementary info).

All polymers were analysed through Gel Permeation Chromatography (GPC) measurements performed on the absolute scale to obtain correct molecular weight distributions (M_w , M_n , M_z , avg, etc.) and the polydispersity of the samples (Table S5, Fig S2 in supplementary info). The solvent used for such measurements was dichloromethane. GPC measurements were performed using a Viscotek dosing and pumping module (currently Malvern Instruments) GPCmax VE 2001, triple detection module (RI, RALS/LALS, IV), Viscotek (now Malvern Instruments) TDA 305, Viscotek detector (now Malvern Instruments) UV Detector 2600, Jordi Resolve DVB Medium MB gel column (300 × 7.8 mm),

eluent—dichloromethane HPLC, flow 1 ml/min, separation temperature and measurement 303 K. Dynamic light scattering measurements were performed on a Malvern Zetasizer equipment to obtain the hydrodynamic radius of polymers of different molecular weights in dilute solutions (see Fig S3 in supplementary info).

3. Results and discussions

3.1. Crossover points and scaling parameters

For all molecular weights and concentrations of PDMS-ethyl acetate systems, extensive viscosity measurements were performed at different temperatures in the range 283–303 K, at every 5 K rise in temperature. According to proposed general scaling theory of de Gennes', initially all the viscosity data were plotted against the ratio of c to c^* , where both the parameters c and c^* were represented in terms of the mass of the polymer per unit volume of the solvent. A clear dependence could be observed in Fig. 1 as expected in theory [3,4]. However the data did not collapse on a single line, especially at very high concentrations. The result of this dependence can be seen in Fig. 1 below. Thereafter, the viscosity scaling paradigm (Eq. (1)) was applied initially, which was originally developed and perfected for semi-dilute systems by Wisniewska et al. [1] shown in Fig. 2. The solutions of low concentration were obeying this relationship to a more satisfactory degree than the higher concentration samples. The representation of Eq. (1) scales the data better than the basic c/c^* scaling of Fig. 1, even though it was also valid. The obtained deviation in the latter part of the semi-dilute zone of the analysis in Fig. 2 (as indicated by the red dotted line) was due to transition to the concentrated zone. Applying Eq. (5), as developed by Cheng et al. [25], we obtain the crossover point c^{**} , which is the position of quantitative change in the structure of the complex liquid as we move into the concentrated zone. Qualitative interpretation of the different local molecular interactions between the monomer and the solvent allows us to broadly categorize the solution under the three concentration zones. In this way, we can identify the transition from semi-dilute to concentrated regime through the molecular fraction of the interacting molecules as:

$$\text{molecular fraction of monomers in solution} > 0.5 \implies c \geq c^{**}$$

We could attribute this to the fact that at such high concentrations, the amount of solvent molecules interacting per monomer unit of the polymer chains in the solution were roughly less than 1–2. This can be seen from the simple depiction in Fig. 3:

Intermolecular interactions of polymer chains in solution [40] are crucial in determining the impact of solvent on the polymer. For lower concentrations, the number of interacting solvent molecules are higher, and therefore the transition from dilute to semi-dilute is governed by the correlation length, as determined by Eq. (4) (the point of hard-sphere polymer coils interactions to entangled coil interactions).

The exponent a in Eq. (1) is a parameter that changes discontinuously at the cross-over to the semi-dilute and concentrated regimes. For PEG–water solutions [9] $a = \beta^{-1}$ for dilute regime and $a = R_h R_g^{-1} \beta^{-1}$ for semi-dilute regime of concentrations. Parameter a is a characteristic for a specific polymer–solvent system, which provides information on the internal structure of any complex liquid [4]. Crossovers between the three regimes of dilute, semi-dilute and concentrated solutions lead to changes in the internal structures, and thereby changes in the value a [2,21,23,41]. Fitting of the Eq. (1) allows us to obtain the different values of a within acceptable deviations as provided in Table 1.

The values are in line with the available literature values for other polymer systems [42] in dilute and semi-dilute systems, with the former reflected as such in good models for polymer systems developed by Wisniewska et al. [1,9] for PEG. Fitting also allows us to obtain the a values for the concentrated zone as well. The obtained data for a remain applicable for PDMS-ethyl acetate systems of all different molecular weights.

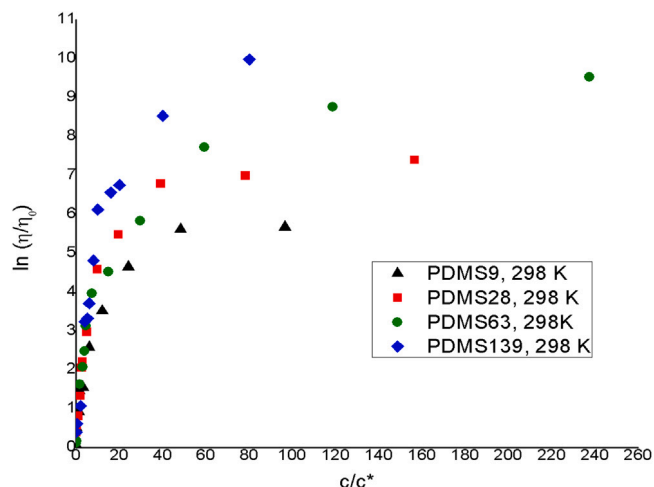


Fig. 1. Results of relative viscosity measurements for PDMS-ethyl acetate solutions plotted against ratio of concentration c to overlap concentration c^* .

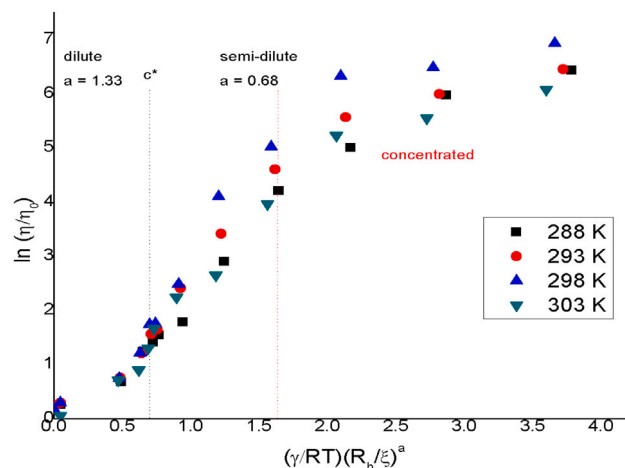


Fig. 2. Initial scaling of viscosity data for PDMS of M_w 28 kg/mol at different temperatures. Only one crossover point c^* was applied (black vertical dotted line). The red vertical dotted line indicated another shift in properties from semi-dilute regime, alluding to the presence of a second crossover c^{**} and the concentrated zone. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

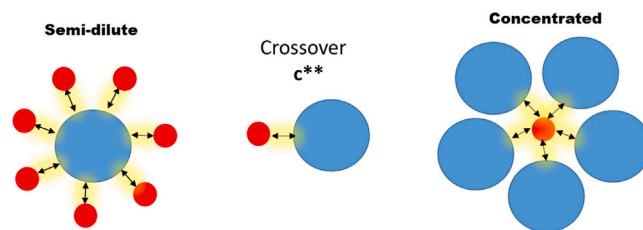


Fig. 3. Crossover point c^{**} from semi-dilute to concentrated regime based on molecular interactions. The \bullet denotes the solvent molecules, while the bigger \bullet denotes the monomers.

3.2. Coil dimensions R_h and R_g vs concentration

The exponent ν (Eq. (3)) from Flory's mean-field theory [16] allows us to obtain the parameter $\beta = 3/4$ which is essential for the correlation length ξ estimation. The correlation length ξ exists only in the entangled zone, and is different to the parameter gyration radius R_g . Generally R_g describes the isolated polymer coil blob size at all

Table 1
Scaling parameter a values for PDMS-ethyl acetate system.

| Scaling parameter a values | | | |
|------------------------------|------------|-------------|--------------|
| Parameter | Dilute | Semi-dilute | Concentrated |
| a | 1.28 | 0.85 | 0.59 |
| Error | ± 0.03 | ± 0.02 | ± 0.02 |

concentrations. At dilute concentrations, polymer coils are treated as hard spheres separate from each other with no impact of local monomer density fluctuations on the coil size; therefore, ξ is more correctly described for dilute solutions as the mean distance of the centre of mass of different neighbouring coils. Correspondingly, this allows for the location of different coils in solution and accounts for the validity of the description of ξ across all three solution regimes, thereby providing an estimate of the blob size even in concentrated and semi-dilute regimes (as postulated by Rubinstein [43]).

Hydrodynamic radius of the coils, R_h , were initially measured at dilute concentrations through dynamic light scattering technique. The data obtained, in conjunction with available literature empirical values, was fit through the scaling equation (Eq. (1)). Generally coil-size (in units of nm) and molecular weights for long chains are related by empirical power law equations of the form [25] (see also Eq. (6)):

$$R_x = KM^y \quad (7)$$

where the parameter R_x is usually described as the gyration or hydrodynamic radius and the constants K and y have values specific to a polymer-solvent system [44–46]. Such results focus on the effects of chain stiffness on the coil sizes at higher concentrations. Based upon the work of Gagliardi et al. [27], the gyration radius R_g is evaluated from Eq. (6), with some minor changes in the coefficient of the power law to compensate for the change in solvent and fitting from the experimental data. Power law relationship for the hydrodynamic radius R_h for PDMS-ethyl acetate systems were harder to determine empirically, due to lack of previous experimental data based on this specific polymer-solvent combination. Starting from the data obtained through dynamic light scattering measurements, within limits of empirical values available for other polymer systems [1] as well as other PDMS-solvent systems [45, 46], the fit of R_h with Eq. (1) formulated the following relation:

$$R_h = (0.0113 \pm 0.001)M_w^{0.57 \pm 0.01} \quad (8)$$

where R_h is determined in nanometres (nm).

In most cases, the coil sizes are assumed constant when considering the structure inside the polymer solutions, even with increasing concentrations. Usually it is as a result of focus on a specific region of polymer concentrations — either in the dilute zone, or up to semi-dilute zone and so on. In the dilute solutions, the polymer coils are separated and far away from each other [6]. Interchain or intrachain interaction effects do not play any part with such low amount of coils in the solution, and so the coil dimensions remain unaffected by any slight change in concentrations. The ratio of the coil dimensions remain as such:

$$\frac{R_h}{R_g} = A, c < c^* \quad (9)$$

where, the parameter A is obtained from Eqs. (6), (8) as:

$$A = \frac{(0.0113 \pm 0.001)M_w^{0.57 \pm 0.01}}{(0.0265 \pm 0.005)M_w^{0.53 \pm 0.02}} \quad (10)$$

Considering that previously established values of R_h/R_g are approximately around 0.6 numerically, our relationship for PDMS-ethyl acetate system maintains the same numerical state. When working with a whole range of polymer solutions from dilute up to polymer melt, it is vital to consider the relative changes that occur in the size of the polymer coils due to concentration changes. R_h and R_g provide us information regarding the hydrodynamic and static screening lengths as

well [6,38]. In the works of Daoud and Jannink [6], as also proposed by Cheng et al. [25], the coil dimensions should decrease with concentration in the semi-dilute and concentrated range, due to screening effects of repulsive intrachain interactions as opposed to interchain interactions. Bennett et al. [38] went further in a similar approach to extend the variation of hydrodynamic screening length fluctuations of polymers in higher concentration solutions beyond c^* . This approach extended to PDMS solutions in other good solvents such as toluene and benzene, predicts a decrease in the static and hydrodynamic screening length with increasing concentration. The ratio of the hydrodynamic to the static screening lengths therefore increase with increasing concentration. However, entire measurements were based on concentrations up to 0.2 g/ml, which is slightly lower than the end of the predicted semi-dilute zone in our data. Dynamic light scattering measurements limit us to concentrations within the dilute or lower semi-dilute zone. All coil dimension changes thereafter are limited to theoretical assumptions based on neutron scattering experiments. Our viscosity data based scaling agrees with the same principle of the concentration fluctuations in the semi-dilute zone. This leads to a slight increase in the coil dimensions in the semi dilute zone, and can be determined by the following proposed relationship:

$$\frac{R_h}{R_g} = Ax^{0.053 \pm 0.005}, c^{**} > c > c^* \quad (11)$$

with x being the mole fraction of the monomer in the solution, and parameter A as obtained from Eq. (10) above. Our predicted exponent for x (approximately 0.053) is slightly lower than that developed by Bennett et al. [38] (approximately 0.15) for other PDMS-solvent systems.

After transition to the concentrated zone, the interactions between the monomer and the solvent reduce to a greater extent than in the semi-dilute zone. The screening effect explained by Bennett [38] or Cheng [25] extends to the concentrated zone, possibly before the onset of the second crossover. However, we believe that the intrachain repulsive interactions are far stronger in the semi-dilute zone than in the concentrated zone. With highly increased polymer concentration, interchain attractive interactions far exceed that of intrachain repulsions, and this congestion of chains inside the solution matrix reduces the hydrodynamic to static screening ratio with increasing concentration, and thereby the R_h/R_g ratio. For simplicity, we assume that beyond the 2nd crossover at higher concentrations, there is a reduction in the coil dimensions:

$$\frac{R_h}{R_g} = Ax^{-0.047 \pm 0.001}, c > c^{**} \quad (12)$$

As the solution reaches closer to the melt characteristics, the coil dimensions reach closer to the initial unperturbed sizes. The above Eqs. (9)–(12) and the values of the constants obtained from them by fitting the experimental viscosity data thereby allow us to have an understanding of concentration on coil dimensions which is fundamental to the study of structure, and motion of polymer coils in good solvents. The parameter R_h is crucial for obtaining the specific polymer-solvent relationship. Our fitted model provides the R_h/R_g ratio, which indirectly also relates to hydrodynamic volume changes proportional to the viscosity as defined under the shear flow (obtained through Eqs (1), (2), and (4)). Crucially, instead of the various factors that influence the chain stiffness, we have tried to provide a simplified model that directly provides the size changes due to such stiffness effects.

3.3. Interaction parameter γ

The interaction related parameter γ proposed by Wisniewski et al. [1] was developed in relation to the Eyring's rate theory [47,48]. It extends the application of the scaling theory for size-dependent complex liquid transportation [49] to obtaining the activation energy for macroscopic viscous flow in such systems. This parameter is usually

Table 2
Interaction parameter γ components for entire PDMS-ethyl acetate solution range.

| Interaction energy parameter γ components | |
|--|-----------------|
| Parameter | Value [kJ/mol] |
| $\gamma_{1,2}$ | 4.00 ± 0.50 |
| $\gamma_{2,2}$ | 2.75 ± 0.50 |

thought to be temperature-independent. However even though the dependence of the parameter on the different molecular interactions present inside a solution have been discussed, the exact nature of the separate interactions were not determined by Wisniewska et al. [1, 9]. Specifically, the amount of these three interactions – monomer–monomer, monomer–solvent and solvent–solvent interactions – determine the effective activation energy required for the viscous flow. It varies due to concentration changes which is represented by the type of interactions. Logically, it is easy to understand that the solvent–solvent molecular interactions will have greater influence on the parameter γ in the dilute zone, the monomer–solvent interactions in the semi-dilute zone and the monomer–monomer interactions in the concentrated zone. The effect of these interaction parameters depends on the mole fractions of each component inside the system and the total parameter γ can be defined by:

$$\gamma = \gamma_{1,2}X_1 + \gamma_{2,2}X_2 \quad (13)$$

where the subscripts 1 denote solvent and 2 denote monomer, and X denotes the mole fraction of the corresponding component. The above equation also takes into consideration that a molecular interaction is created through a pair of molecules. The solvent viscosity η_0 used in Eq. (1) is an indicator of the solvent–solvent interactions, so the above equation for γ does not contain the parameter $\gamma_{1,1}$. By the same fitting applied to Eq. (1) and from the results depicted in Fig. 4 before, we obtain estimates of the individual interaction parameters provided in Table 2.

The subscripts 1, 2 indicate the solvent–monomer interaction parameter, which as stated before is the dominant interaction in the semi-dilute zone, and any changes in the overall energy is influenced by $\gamma_{1,2}$ values during the fitting procedure, while the other interactions are considered constant. This is maintained accordingly for the concentrated zone with $\gamma_{2,2}$. In the fitting for the dilute zone, both interaction parameters are maintained constant. The effect of the pure solvent–solvent interactions are considered through the pure solvent viscosity η_0 . From the information of Table 2, it can be clearly calculated through Eq. (13) that the overall γ varies around 3.40 ± 0.50 kJ/mol across all range of mole fractions for all the molecular weights. It is very similar to the energy required in literature [1,9] for the viscous motion of various other polymer solutions.

3.4. Data fitting

Proper understanding and application of the different parameters in Eq. (1) provided us with the final well-fitted curve of the scaling paradigm as shown in Fig. 4 below. The parameter ν relating the radius of gyration to the molecular mass $R_g \sim M_w^\nu$ is determined from the mean-field theory and is indicative of the repulsive excluded-volume interactions and the corresponding relationships are expressed through Eqs. (2)–(3).

3.5. Connectivity to established scaling laws

Wisniewska et al. [1] probed further into the applicability of this form of scaling Eq. (1) when taking into consideration the equations already available in various forms from older literature such as that of Martin [31] and Huggins [30]. There have also been equations specific to PDMS based systems as developed by Warrick et al. [50]

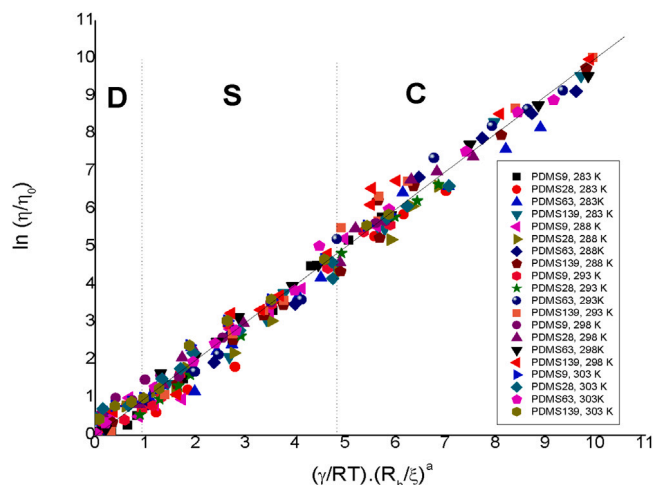


Fig. 4. Viscosity scaling including the temperature dependence and the shift of parameters at different crossovers. The labels 'D' represents the dilute regime, 'SD' the semi-dilute regime and 'C' the concentrated regime, with the dotted lines in-between representing the cross-over points c^* and c^{**} respectively.

and Kolorlev et al. [51]. These equations have the basic form of the relationship for viscosity of polymer solutions as:

$$\eta = \eta_0(1 + c[\eta]) \quad (14)$$

where $[\eta]$ is the intrinsic viscosity. As mentioned before, for the non-entangled regime (dilute solutions), $a = \beta^{-1}$, and the general form of Eq. (1) boils down to:

$$\eta = \eta_0 \left[1 + \frac{\gamma_{1,2}}{RT} \left(\frac{R_h}{R_g} \right)^a \frac{c}{c^*} \right] \quad (15)$$

where we consider only the first term of the series when the exponential function in Eq. (1) is expanded. This shows that our scaling equation has the same form as Eq. (14) when considered in the same limits of low concentrations for solutions. Eqs. (14) and (15) are of the same general form, and the intrinsic viscosity is expressed as:

$$[\eta] = \frac{\gamma_{1,2}}{RT} \left(\frac{R_h}{R_g} \right)^a \frac{1}{c^*} \quad (16)$$

This form also follows the general trend shown in literature for the inverse relationship between intrinsic viscosity and overlap concentration c^* , as per the Mark–Houwink equation [52–54]. Easy estimations of the intrinsic viscosity for polymer dilute solutions can be made through Eq. (16). Further expansion terms of the exponential series in Eq (1) would reveal more accurate formulas that would be analogous to the general used form of the Huggins equation [30]. The relationship established through Eq. (1) can therefore be postulated for a wide variety of scenarios related to characterization and analysis of polymer solutions in all regimes.

Finally, the viscosity under slow flow is equivalent to an integral of the relaxation modulus $G(t)$ with respect to the time [55]. Namely, the dynamics of polymer chains reflected in $G(t)$ determines the viscosity, which results in significant molecular weight (M) dependence of $G(t)$ and viscosity. Such effects of viscoelasticity can be expected to be present at highly concentrated polymer solutions. However, the fact that purely macroscopic viscous Newtonian flow could be observed in our experiments was more significant from our perspective, since it was in line with our scaling model theory.

4. Conclusions

We have shown that the viscosity scaling form previously established for aqueous PEG solutions can also be applied to solutions of

PDMS in ethyl acetate. Furthermore, we have extended the previous form that was applicable mostly to dilute and semi-dilute concentration ranges, so that it now includes the concentrated regime of polymer solutions.

Two clear crossovers between the concentration regimes were observed, as represented by the c^* and c^{**} . These cross-over points not only lead to change in the scaling parameters, but also in the system properties such as the coil dimensions. Scaling parameters were found to change in the same order as for other reported polymer systems. Coil dimension model on the other hand was carefully developed to ensure that effects of concentration changes, chain interactions, repulsion and screening effects were considered to determine a more accurate picture of the internal structure of the polymer–solvent system. These observations reestablish the fact that the rheological characteristics of complex systems are heavily governed by the volume occupied by the macromolecules as well as the dynamic molecular structures formed by them.

In Eq. (1), we have a form of applicable characterization of the viscosity of polymer solutions. This approach is applicable for a broad range of concentrations, molecular weights, temperatures as well as showcasing its use for all types of standard and non-standard grade polymers. This expands the usability of the approach from pure academic research to useful processing applications in industrial level, with focus on commercially used polymers. Most researches are based on highly monodispersed samples. However, synthesis of such monodispersed polymers at amounts above 10–100 g are impossible, and corresponding theories have few benefits in large scale-applications. By using commercially available polymers, the overall impact of obtaining a general scaling model applicable for huge amounts of commercially available polymers is highly significant, even accounting for some data scattering.

The proposed approach has been developed based on common polymer characterization notions: hydrodynamic and gyration Radii, correlation length and Flory exponents. Every parameter appearing in the approach has been properly interpreted, and any changes due to crossovers has been recognized. Through power series expansion of the exponential equation of the applied scaling approach, the theory can also be reduced to the simplistic approach used to describe dilute polymer solutions [30,31,52–54], thereby providing means to obtaining the intrinsic viscosity of polymer solutions. Previously developed notions of viscous flow as an activated energy process [1,9,49] have been successfully re-evaluated to obtain information regarding the various molecular interactions occurring locally in polymer solutions.

We developed our conclusions after performing precise viscosity measurements through accurate techniques for a model good solvent system: PDMS in ethyl acetate. Based on previously well established scaling model, this investigation shows that it can be further enhanced to cover more extensive complex systems. Literature data [1,7,9,25,27,38] supports the validity of our proposed physical approach, in conjunction with curves obtained from our own experimental results. It brings us closer to a more universal and uniform characterization method for all types of polymer systems with increased commercial usage.

CRedit authorship contribution statement

Airit Agasty: Formal analysis, Investigation, Methodology, Writing - original draft. **Agnieszka Wisniewska:** Investigation, Methodology, Supervision. **Tomasz Kalwarczyk:** Writing - review & editing. **Kaloian Koynov:** Supervision, Writing - review & editing. **Robert Holyst:** Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.polymer.2020.122779>.

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