

**Revisiting experimental techniques and theoretical models for estimating the solubility
parameter of rubbery and glassy polymer membranes**

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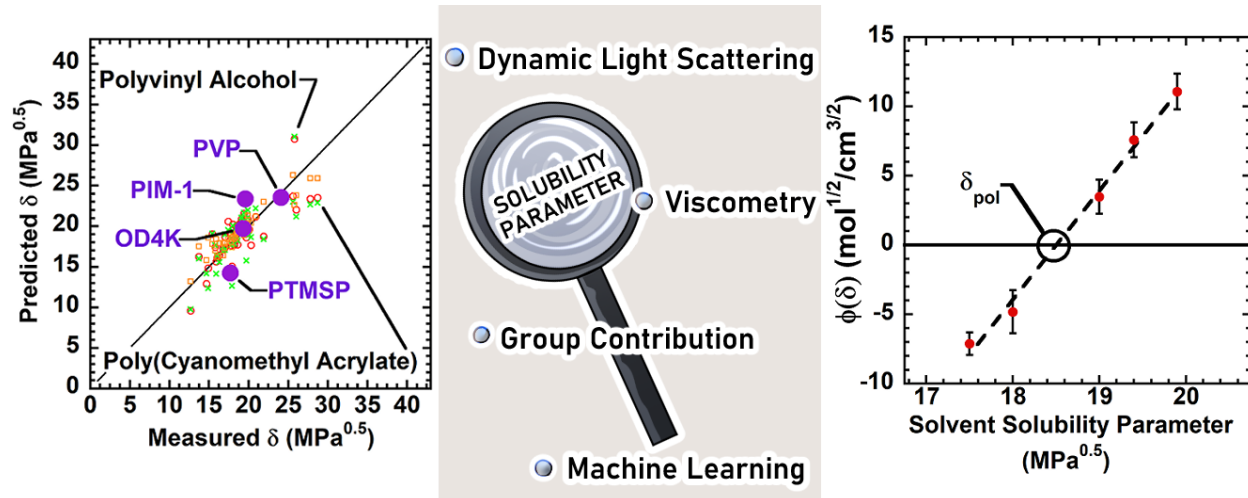
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Graphical Abstract



Highlights

- DLS was used as a novel route to evaluate the solubility parameter of polymers.
- DLS results exhibit good agreement with viscometry and group contribution methods.
- Group contribution parameters were updated using accurate polymer van der Waals volumes.
- Experiments provide more accurate estimates of microporous polymers solubility parameters than group contribution.
- Machine learning models suggest no changes to group contribution are needed.

Abstract

Estimation and correlation of the Hildebrand solubility parameter (δ) of polymers and small molecules is a common practice in membrane material science and is accomplished by experimental and numerical routes. In this paper, we revisit, update, and compare both routes to enhance the accuracy in the determination of δ . Best practices for the experimental determination of polymer solubility parameters are provided, and the viability of Dynamic Light Scattering (DLS) was demonstrated as an alternative to conventional time- and material-consuming techniques, such as Ubbelohde viscometry and swelling measurements. Glassy and rubbery polymers, including high fractional free volume (FFV) microporous polymers such as PIM-1 and poly(1-trimethylsilyl-1-propyne) (PTMSP), are among the samples included in this study with great relevance to membrane science. In an attempt to enhance the accuracy of numerical estimate of polymer solubility parameters via the group contribution method, we provide updated group contribution parameters, along with their uncertainty, according to the technique recently reported by Smith et al. These updated group contribution parameters result in a mean absolute relative error of 9.0% in predicting the solubility parameter on a test set of 40 polymers, which is on par with the average 10% error reported previously. We also show, using machine learning techniques, that augmenting the group contribution model with extra parameters or non-linear relationships does not improve its accuracy. Results of the updated group contribution technique and dynamic light scattering measurements were compared to experimental viscometry on four test polymers, and the difference between the three techniques is compared.

Keywords:

Polymer solubility parameter; light scattering; group contribution; machine learning

1. Introduction

The Hildebrand solubility parameter, δ , is used to predict and correlate miscibility among substances, including low molecular weight compounds and polymers [1–4], and is used in practical applications such as coatings [5,6], drug delivery [7,8], material formulation [9], and membrane separations [10–15]. A general rule-of-thumb is that the solubility parameter of a good solvent should depart by no more than $\pm 2 \text{ MPa}^{0.5}$ from that of the polymer [16]. It is well known that the sorption of gases and liquids in polymers decreases linearly with the squared difference between the penetrant and polymer solubility parameters [12]. Due to this, liquid solvent flux through organic solvent nanofiltration (OSN) and organic solvent reverse osmosis (OSRO) membranes exhibits systematic correlations with the polymer and penetrant solubility parameters [10–13]. Burgal et al. found a strong correlation between the molecular-weight cutoff of nanofiltration membranes and the solubility parameter of solvents used in the post-fabrication treatment [14]. The solubility parameter was also used to rationalize negative retention behavior in OSN experiments [15]. These examples indicate that knowing the solubility parameters with sufficient accuracy is essential to develop structure-property correlations in membrane material science.

The solubility parameter of a pure species i is defined as follows:

$$\delta = \sqrt{\frac{E_{coh}}{V_m}} \quad (\text{Eq. 1})$$

where E_{coh} and V_m are the cohesive energy and the molar volume of the pure species i , respectively. The δ values are normally provided at 298.15K. The solubility parameter of small molecules correlates directly with their enthalpy of vaporization and molar volume (cf. Eq. 2), both of which can be experimentally measured [17]:

$$\delta = \sqrt{\frac{\Delta H_{vap} - RT}{V_m}} \quad (\text{Eq. 2})$$

where ΔH_{vap} is the molar enthalpy of vaporization, R is the ideal gas constant, and T is the absolute temperature at which enthalpy is measured. Polymers, however, do not have a measurable enthalpy of vaporization, so indirect methods have been developed to estimate their solubility parameter.

The two conventional experimental and modeling approaches used to estimate the solubility parameter of polymers are solvent-polymer interaction experiments (e.g., viscometry [18], swelling measurements [19,20]) and extrapolation of small molecule data through group contribution methods [17], respectively. Experimental methods, while providing a direct measure of the solubility parameter, can be time consuming. In contrast, theoretical techniques offer a more efficient approach for predicting solubility parameters. In recent years, machine learning (ML) techniques have been used to predict material properties, which use large datasets to accurately predict glass transition temperature (T_g), solubility parameter, and density, just to mention a few [21].

In this study, we introduce the use of dynamic light scattering (DLS) as a new, rapid experimental route to measure the solubility parameter of polymers. Of equal importance, we updated the solubility parameter group contribution values to be consistent with recent improvements in van der Waals volume estimates [22] while providing, for the first time, the analytical error associated to each contribution. This study seeks to enhance the accuracy of solubility parameter measurements, enabling the formulation of more reliable structure-property correlations in membrane science. Thus, this paper will *i*) verify and compare experimental and theoretical approaches using both well-studied (polyvinylpyrrolidone) and newly synthesized (OD4K) polymers, and *ii*) extend the proposed approach to relevant polymers used in membrane science, including polymer of intrinsic microporosity (PIM-1) and poly(1-trimethylsilyl-1-propyne) (PTMSP).

2. Experimental Methods and Materials

2.1 Intrinsic Viscosity and Dynamic Light Scattering Measurements

Details about chemicals and polymers used in this study are provided in the Supporting Information (SI), Section 1-3. Intrinsic viscosity of four polymers, polyvinylpyrrolidone (PVP), OD4K, PTMSP, and PIM-1 (cf. SI, Section 3), was measured in a variety of solvents using Ubbelohde viscometers. Additionally, the hydrodynamic diameter (D_h) of PVP, OD4K, PTMSP, and PIM-1 in a variety of solvents was measured using dynamic light scattering. Both the intrinsic viscosity and hydrodynamic diameter for each polymer was plotted against the solvent solubility parameter, to elucidate any correlation. Experimental data was elaborated using the method outlined by Mangaraj [24] (cf. SI, Sections 4-5), to accurately determine the solubility parameter

value of each polymer. Details about intrinsic viscosity and hydrodynamic diameter measurements are provided in the SI, Sections 6 and 7, respectively. For the sake of brevity, PTMSP data are shown in the Supporting Information (cf. SI, Section 8)

2.2 Group Contribution Method and Machine Learning

The group contribution technique defines the solubility parameter, δ , as follows:

$$\delta = \frac{\sum_{i=1}^n F_i}{V_W} \quad (\text{Eq. 3})$$

where F_i is the contribution of each functional group in the molecule to the total molar attractive force, the sum of which is normalized by the molecule's van der Waals volume (V_W). In this work, V_W is calculated using contributions from each functional group ($V_{W,i}$), along with the overlap volume ($V_{overlap,j}$) between neighboring functional groups, as described by Wu et al. (cf. Eq. 4), to increase the accuracy of the volume predictions and, by extension, the group contribution values [22].

$$V_W = \sum_{i=1}^n V_{W,i} - \sum_{j=1}^m V_{overlap,j} \quad (\text{Eq. 4})$$

This specific method is then used to compare viscometry and DLS techniques, while simultaneously providing updated molar attractive force contribution fittings. The updated group contribution fittings can be found in SI, Section 9, along with example calculations (cf. SI, Section 10), as well as the optimization strategy and error estimation (cf. SI, Section 11). Details about the machine learning model are provided in the SI, Section 12.

3. Results and Discussion

3.1 DLS and Viscometry Comparisons

Intrinsic viscosity, as well as swelling measurements, are commonly used to study polymer interactions with solvents and determine their molecular weight [17]. The solvent in which a polymer attains the largest intrinsic viscosity normally exhibits a solubility parameter closest to that of the polymer. As the solubility parameter of the solvent deviates from that of the polymer, interactions between the polymer and solvent become unfavorable, causing polymer chains to become more coiled and compact. This well-documented technique [18,20,25] was used to estimate the solubility parameter of our baseline polymer, PVP, whose properties have been reported previously [26]. PVP exhibited the highest intrinsic viscosity (i.e., 0.433 dL/g) in

acetonitrile ($24.4 \text{ MPa}^{0.5}$) (cf. Figure 1A). Fitting the information from Figure 1A to equation S3 and constructing the corresponding Mangaraj plot (cf. Figure 1B), results in the fitted theoretical maximum intrinsic viscosity ($\eta_{int,max}$) value of 0.435 dL/g , which provides, for PVP, a solubility parameter of $24.1 \pm 0.39 \text{ MPa}^{0.5}$. Since a limited number of solvents was used for the experimental campaign, locating the position of the true maximum for the intrinsic viscosity as a function of the solvent solubility parameter may be somehow arbitrary and lead to significant errors. In contrast to just using the maximum from Figure 1A, the Mangaraj method (cf. SI sections 4 and 5) can suggest polymer solubility parameters intermediate to those of the solvents used, serving as a recommended method for a reliable data elaboration.

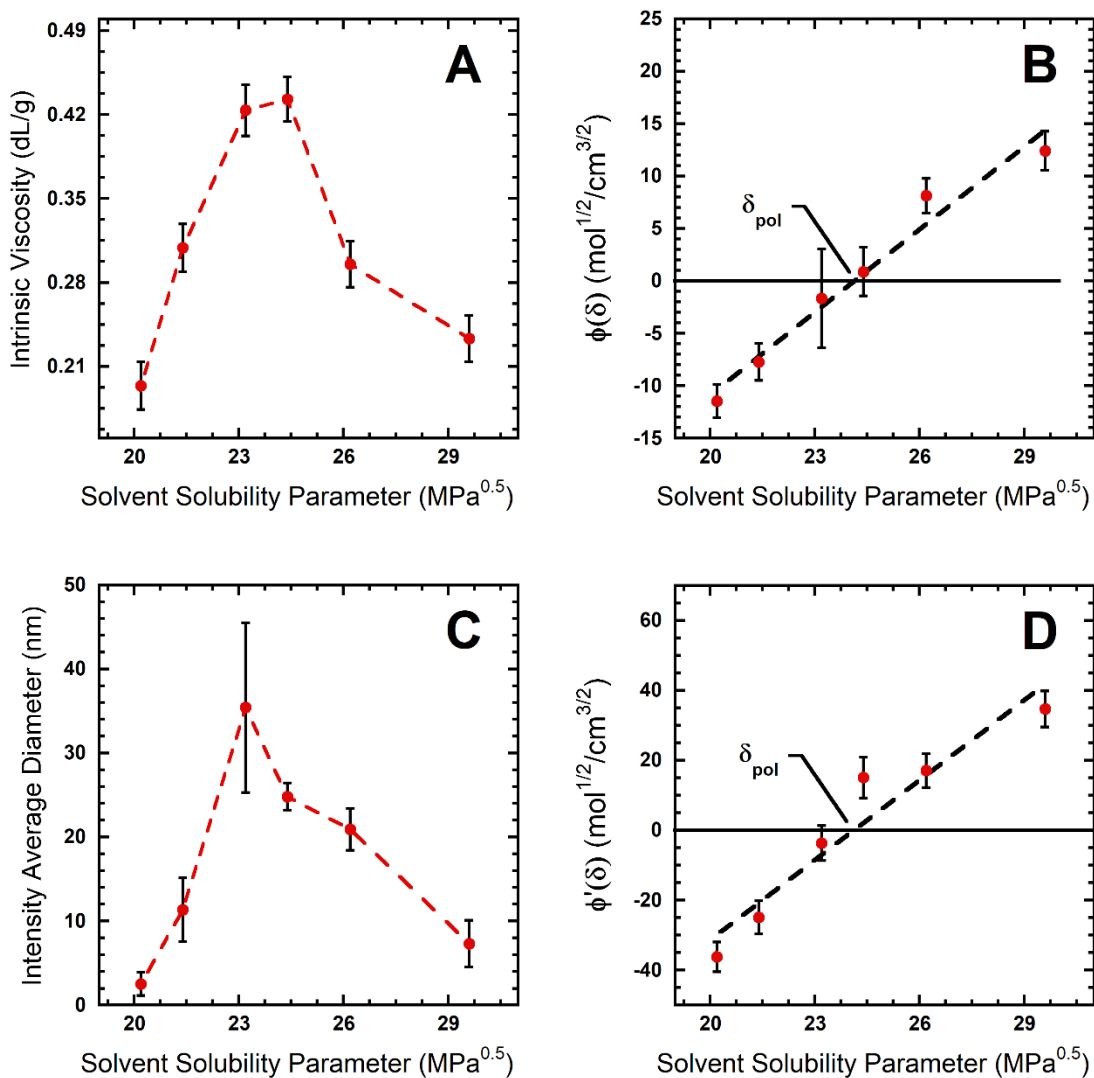


Figure 1: A) Intrinsic viscosity of PVP as a function of the solvent solubility parameter at 25°C (lines serve to guide the eye). B) Intrinsic viscosities are used to generate the Mangaraj plot, where ϕ is plotted as a function of solvent solubility parameter for PVP. C) Intensity average diameter of PVP, obtained from DLS measurements, as a function of the solvent solubility parameter at 25 °C (lines serve to guide the eye). D) Intensity average diameters are used to generate the Mangaraj plot, where ϕ' is plotted as a function of solvent solubility parameter for PVP. The linear best fit line for both plots in B $\{2.6x - 63.5, R^2 = 0.97\}$ and D $\{y = 7.6x - 183.9, R^2 = 0.92\}$ are shown. Uncertainty values were calculated through repeated measurements (A and C) and linear error propagation (B and D).

The experimental route mentioned above, however, requires viscosity data in numerous solvents at various concentrations, and therefore it is time and material consuming, which may be problematic when working with non-commercial, expensive polymers. Dynamic light scattering may offer a quicker route while consuming less material. DLS can indirectly provide information about solubility parameters by measuring the size of polymers in different solvents. Analogous to viscometry techniques, the solvent in which a polymer attains the maximum hydrodynamic diameter (i.e., maximum swelling), has a solubility parameter closest to that of the polymer. To test the applicability of DLS in this scenario, the solubility parameter of PVP, as estimated from the intrinsic viscosity ($\sim 24.1 \text{ MPa}^{0.5}$), was compared to that estimated using DLS (cf. Figure 1C). PVP experienced a maximum swelling (i.e., hydrodynamic size $\sim 35.4 \text{ nm}$) in butanol ($23.2 \text{ MPa}^{0.5}$), which aligns well with the values previously reported in the literature (i.e., $22.2 - 26.3 \text{ MPa}^{0.5}$) [27–29] estimated by various group contribution methods. The Mangaraj analysis (cf. Figure 1D) provides, for PVP, a solubility parameter equal to $24.1 \pm 0.27 \text{ MPa}^{0.5}$ ($D_{h,\max} = 36.9 \text{ nm}$). The excellent agreement between the two approaches, depicted for the case of PVP, serves to validate the use of DLS for this purpose.

The proposed approach was then used to estimate the intrinsic viscosity and hydrodynamic diameter for OD4K, a newly synthesized poly(amic acid) [23], as a test case. According to Ubbelohde viscosity measurements, this polymer experiences the greatest intrinsic viscosity (0.268 dL/g) in CHCl_3 ($19 \text{ MPa}^{0.5}$) (cf. Figure 2A). The Mangaraj fitting (cf. Figure 2B) yields an $\eta_{\text{int},\max}$ value of 0.286 dL/g , with a corresponding solubility parameter of $18.6 \pm 0.07 \text{ MPa}^{0.5}$. This value was then compared to the DLS approach. OD4K experienced a maximum swelling (i.e., hydrodynamic diameter $\sim 2.5 \text{ nm}$) in acetone ($19.9 \text{ MPa}^{0.5}$) (cf. Figure 2C). Using the Mangaraj fitting (cf. Figure 2D), $D_{h,\max}$ is estimated to be 2.52 nm , with a corresponding solubility

parameter of $19.9 \pm 0.08 \text{ MPa}^{0.5}$. As in the case of PVP, the solubility parameter of OD4K found using DLS and viscometry are in close agreement, specifically, within 8% of one another.

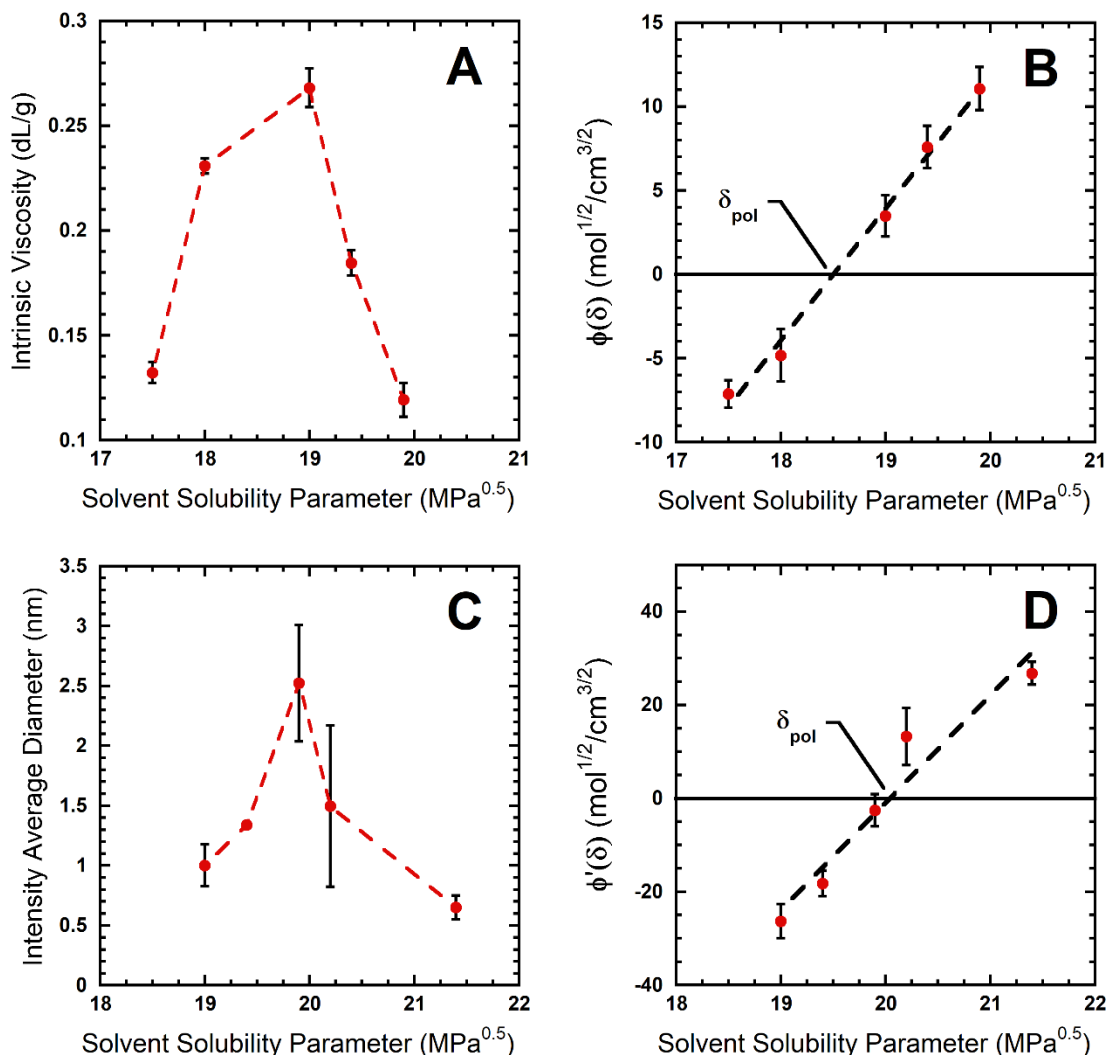
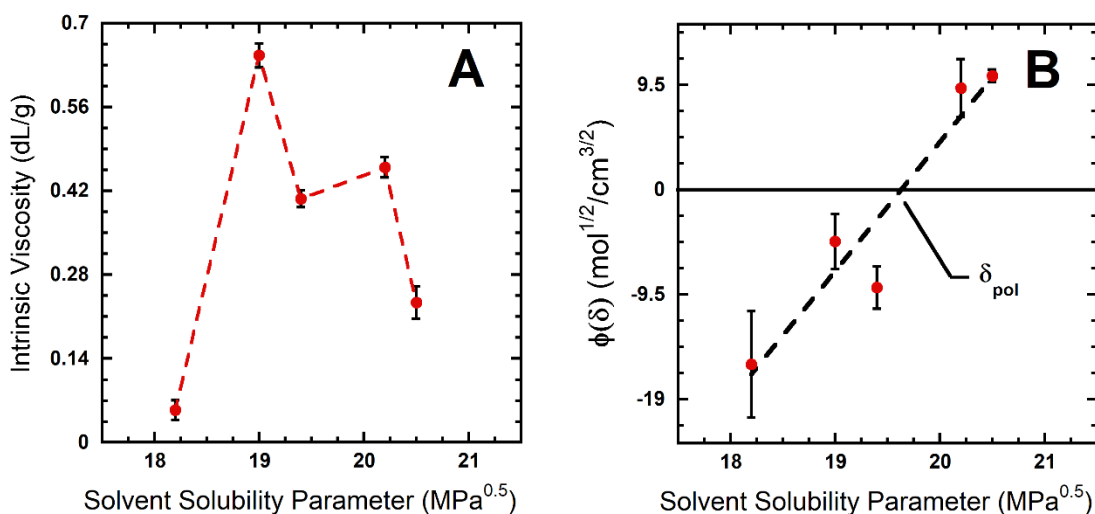


Figure 2: A) Intrinsic viscosity of OD4K as a function of the solvent solubility parameter at 25°C (lines serve to guide the eye). B) Intrinsic viscosities are used to generate the Mangaraj plot, where ϕ is plotted as a function of solvent solubility parameter for OD4K. C) Intensity average diameter of OD4K, measured via DLS, as a function of the solvent solubility parameter at 25°C (lines serve to guide the eye). D) Intensity average diameters are used to generate the Mangaraj plot, where ϕ' is plotted as a function of solvent solubility parameter for OD4K. The linear best fit line for both plots B $\{y = 7.8x - 145.2, R^2 = 0.98\}$ and plot D $\{y = 20.2x - 401.7, R^2 = 0.94\}$ are shown. Uncertainty values were calculated through repeated measurements (A and C) and linear error propagation (B and D).

PIM-1, a high T_g (> 430 °C [30]), high FFV ($28.5 \pm 0.5\%$, calculated using density from ref. [31]) microporous polymer, was included in this study (cf. Figure 3) to further assess the validity of the newly proposed methodology. Specifically, PIM-1 was selected for being a material of great interest in membrane science. PIM-1 exhibits the highest intrinsic viscosity (0.646 dL/g) in CHCl_3 ($19.0 \text{ MPa}^{0.5}$) (cf. Figure 3A). Fitting the viscometry data to the Mangaraj plot (cf. Figure 3B) provides a solubility parameter of $19.6 \pm 0.09 \text{ MPa}^{0.5}$ with a fitted maximum intrinsic viscosity of 0.772 dL/g. Likewise, the DLS data for PIM-1 (cf. Figure 3C) exhibits a trend identical to the intrinsic viscosity measurements, with the polymer attaining the largest hydrodynamic diameter (40.7 nm) in CHCl_3 . The Mangaraj fitting on the DLS data for PIM-1 (cf. Figure 3D) yields a solubility parameter of $19.5 \pm 0.19 \text{ MPa}^{0.5}$, with a fitted maximum hydrodynamic diameter of 42.3 nm. Remarkably, also in the case of PIM-1 the agreement between viscometry and DLS data is excellent.



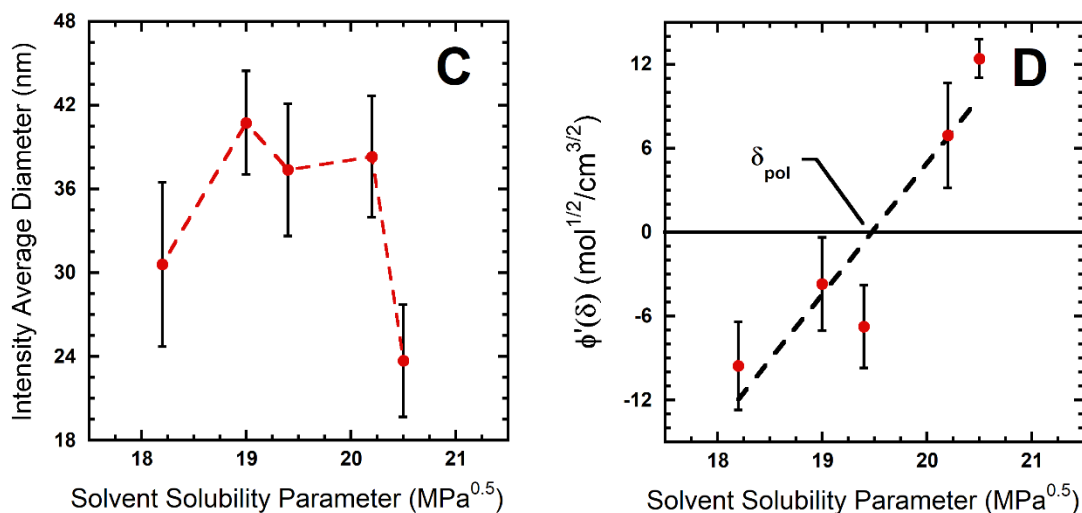


Figure 3: A) Intrinsic viscosity of PIM-1 as a function of the solvent solubility parameter at 25°C (lines serve to guide the eye). B) Intrinsic viscosities are used to generate the Mangaraj plot, where ϕ is plotted as a function of solvent solubility parameter for PIM-1. C) Intensity average diameter of PIM-1, measured via DLS, as a function of the solvent solubility parameter at 25°C (lines serve to guide the eye). D) Intensity average diameters are used to generate the Mangaraj plot, where ϕ' is plotted as a function of solvent solubility parameter for PIM-1. The linear best fit line for both plots B $\{y = 11.7x - 229.8, R^2 = 0.90\}$ and plot D $\{y = 9.4x - 182.5, R^2 = 0.86\}$ are shown. Uncertainty values were calculated through repeated measurements (A and C) and linear error propagation (B and D).

Intrinsic viscosities and hydrodynamic diameters for PIM-1 in tetrahydrofuran (THF) (19.4 MPa^{0.5}) tend to somehow negatively deviate from the generally observed trend (cf. Fig. 3B-D). These deviations are ascribed to the presence of trace water in the solvent, as it was observed that the measured hydrodynamic diameter for PIM-1 increases in size by 25.7% when using HPLC-grade THF relative to the hydrodynamic diameter obtained when using non-HPLC grade THF. This deviation does not appear to affect the accuracy of the fitting, though. Indeed, the obtained solubility parameter value for PIM-1 (19.5 MPa^{0.5}) agrees with previously reported experimental values (19.0 MPa^{0.5} [32], 19.5 MPa^{0.5} [33]). Also in the case of PTMSP, another high T_g [34], high FFV polymer [35] a very good agreement between viscometry and DLS data was observed. For the sake of brevity, PTMSP results are shown in the SI, section 8. Thus, the experimental techniques presented in this study can be successfully used to determine the solubility parameters of modern membrane materials exhibiting rigid, bulky, and contorted monomer structures, other than rubbery polymers and low free volume glassy polymers.

3.2 Revisiting the Group Contribution Method

As stated earlier, the overarching goal of this study is to provide methods for fast, accurate, and reliable estimates of polymer solubility parameters. In the previous section, we proposed a new experimental method to accomplish this goal. Another important question is: *can group contribution method validate DLS measurements as a technique to estimate the solubility parameter?* In this section, we answer this question by first updating group contribution parameters and then comparing the predictions made by these new parameters to the experimental data shown in section 3.1. Finally, a neural network was used to test whether improvements may be made to the prediction of solubility parameters when given the same set of data as the group contribution model. The aim of implementing the neural network herein is to use it as a tool to probe if augmentations to the group contribution techniques could be made. If there is a better way to correlate the molar volume and functional group identity than group contribution, the neural network should *per se* have a significantly lower prediction error than the group contribution technique. This is due to the neural network containing more adjustable parameters than group contribution (which uses one parameter per functional group) and having capability to approximate complex non-linear relationships [36].

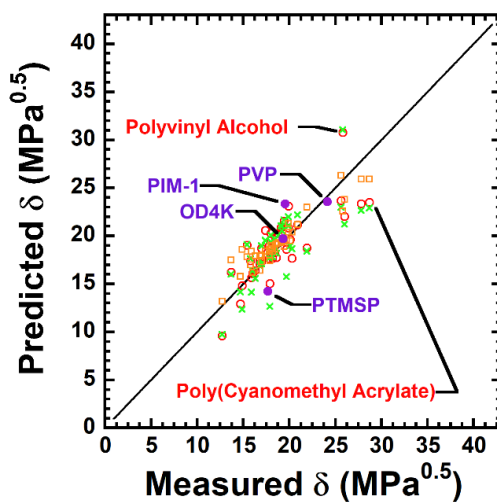


Figure 4: Parity plot of predicted vs. measured polymer δ , in units of MPa^{0.5}. Red symbols are group contribution predictions, green symbols are neural network predictions, and yellow symbols are predictions from the Polymer Genome Project [21]. Polymer genome is the state-of-the-art machine learning tool, therefore it is reported separately. Purple symbols indicate group contribution predictions of PVP, OD4K, PTMSP, and PIM-1 versus the solubility parameter determined experimentally in this work.

Experimentally determined solubility parameters of 40 polymers (cf. SI, Section 13) were taken from a variety of literature sources and used to validate the group contribution and neural network performance [17,37]. Using the updated group contribution parameters, a mean absolute relative error (MARE) of 9.0% was achieved on the polymer dataset (cf. Figure 4 and Table S4), which is in line with the error of previous group contribution estimates [17]. Thus, using the higher accuracy molar volume predictions provided by Wu et al. [22] did not result in improved solubility parameter predictions.

Predicted and measured solubility parameter values from both group contribution and the neural network are compared in Figure 4. Both techniques gave similar predictions, and the MARE of the group contribution (9%) and neural network (10.3%) are nearly identical. Highly polar polymers, such as poly(cyanomethyl acrylate), PVA, and Nylon (6,6) tend to deviate from the parity line (16-18% error, cf. Figure 4), while predictions for nonpolar polymers, such as poly(methyl octyl siloxane), polyisobutylene, and PDMS (1% error), tend to be more accurate. This could be interpreted as error increasing with the magnitude of the solubility parameter itself, as polar molecules tend to have larger solubility parameters than nonpolar ones. Thus, the solubility parameter of polar polymers should possibly be determined experimentally to achieve adequate accuracy, for example via viscometry or DLS measurements.

An important implication of this modeling effort is that the neural network and the group contribution solubility parameter predictions do not differ significantly (cf. Figure 4, Table S4). This finding suggests that group contribution performs optimally in the case of extrapolating a set of small molecule solubility parameters to polymers, and that augmentation to the group contribution technique (via new correlations between base functional groups) would not further improve its accuracy. Further discussion about the insights gained from the machine learning model can be found in SI, Section 14. Also, it should be noted that machine-learning models in materials science, such as the *Polymer Genome Project* [21], use information beyond just functional groups, such as topological polar surface area, van der Waals surface area, and other quantitative structure-property parameters. Consistently, *Polymer Genome* outperforms group contribution when making polymer solubility parameter predictions (MARE = 5.8%, cf. Figure 4 and Table S4). Therefore, if future improvements to group contribution models are to come, they will likely require additional types of information such as the ones used in *Polymer Genome*. Thus,

it makes sense that the group contribution technique has not seen much improvement since its inception. Despite this shortcoming, the group contribution technique has remained a prevalent method for estimating polymer solubility parameters due to its acceptable performance and ease-of-use.

3.3 Comparison of Experimental and Numerical Results

Comparisons of viscometry, DLS, and group contribution in obtaining the solubility parameters of PVP, OD4K, PTMSP, and PIM-1 are shown in Table 1. For PVP, estimates from the three techniques are within error of each other. Of note, DLS and viscometry gave exactly equal values of PVP’s solubility parameter. The solubility parameter of OD4K estimated from all three techniques exhibit a larger spread, with a difference among estimates close to 10%. For PIM-1 and PTMSP, numerical estimates exhibit larger deviations from the experimentally measured values, with group contribution predicting $23.36 \pm 0.68 \text{ MPa}^{0.5}$ for PIM-1 (19.2% error) and $14.24 \pm 0.55 \text{ MPa}^{0.5}$ for PTMSP (18.6% error). These deviations underpin the need for more experimentally determined solubility parameters of modern microporous membrane materials, such that more accurate predictive models can be constructed. A more detailed discussion regarding the origin of these deviations and the performance of the group contribution and machine learning models in predicting the solubility parameters of polyimides, another class of polymers relevant to membrane science, is provided in Section 8, SI.

Table 1: Summary of PVP, OD4K, PIM-1, and PTMSP solubility parameters in units of $\text{MPa}^{0.5}$. The solubility parameter for OD4K, PVP, PIM-1, and PTMSP was estimated using the Mangaraj analysis of experimental viscometry and DLS data. Solubility parameters estimated using the updated group contribution method (cf. Eq. 3) have also been included.

<i>polymer</i>	<i>viscometry method</i>	<i>DLS method</i>	<i>group contribution</i>
<i>PVP</i>	24.1 ± 0.39	24.1 ± 0.27	23.6 ± 0.29
<i>OD4K</i>	18.6 ± 0.07	19.9 ± 0.08	19.7 ± 0.27
<i>PIM-1</i>	19.6 ± 0.09	19.5 ± 0.19	23.36 ± 0.68
<i>PTMSP</i>	17.8 ± 0.15	17.5 ± 0.14	14.24 ± 0.55

Interestingly, the maximum relative error in the solubility parameters determined using DLS and viscometry was 8.1%, which is close to the group contribution technique's MARE of 9.0%. Since the group contribution technique was trained on experimental data, it is not unreasonable to assign an expected error of approximately $\pm 10\%$ for both experimental measurements and group contribution. This magnitude of error may at first appear to disagree with the error bars listed in Table 1, which show a relative error below 2%. However, this result no longer appears contradictory when considering that the error bars from both experimental measurements and group contribution better reflect the solubility parameter's *precision* rather than its *accuracy*. That is, the error bars reflect the range of expected solubility parameters that would be estimated if viscometry or DLS experiments were to be repeated multiple times, *not* what the estimates are with respect to the true solubility parameter. These error bars do not reflect inherent errors such as instrumental bias, human error, and other systematic errors.

4. Conclusions

In this study, dynamic light scattering, viscometry experiments, and numerical polymer solubility parameter estimation techniques were compared, discussed, and updated. First, we presented viscometry measurements to ensure reliable assessment of the polymer solubility parameter. Then, DLS was validated as an alternative experimental technique for a rapid estimation of polymer solubility parameters relative to Ubbelohde viscometry and swelling measurements, while still maintaining adequate accuracy. Also, a data elaboration procedure, based on the Mangaraj's method, was validated to achieve the best estimates from experimental measurements. For numerical estimates of the polymer solubility parameter, updated group contribution parameters featuring parameter uncertainties were provided, and group contribution was compared to machine learning techniques. Both approaches performed similarly when fit to the same data, suggesting that group contribution does not have room for augmentation unless additional molecular-level data are incorporated. DLS and the updated group contribution technique provided solubility parameter estimates of the test polymers (PVP, OD4K, PIM-1, and PTMSP) and were compared with viscometry, an established technique. Additionally, insights are provided explaining why some classes of polymers are predicted more readily via group contribution, which resides primarily in the presence of adequate training data. From a membrane science perspective, having accurate solubility parameter estimates should, in principle, improve the self-consistency

of transport and fabrication correlations both within individual studies and in meta-analyses made using large bodies of data from various researchers.

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References

- [1] N.M. Larocca, L.A. Pessan, Effect of antiplasticisation on the volumetric, gas sorption and transport properties of polyetherimide, *Journal of Membrane Science*. 218 (2003) 69–92. [https://doi.org/10.1016/S0376-7388\(03\)00139-X](https://doi.org/10.1016/S0376-7388(03)00139-X).
- [2] C.M. Hansen, Polymer additives and solubility parameters, *Progress in Organic Coatings*. 51 (2004) 109–112. <https://doi.org/10.1016/j.porgcoat.2004.05.003>.
- [3] J.S. Lee, J. Leisen, R.P. Choudhury, R.M. Kriegel, H.W. Beckham, W.J. Koros, Antiplasticization-based enhancement of poly(ethylene terephthalate) barrier properties, *Polymer*. 53 (2012) 213–222. <https://doi.org/10.1016/j.polymer.2011.11.006>.
- [4] S. Zekriardehani, A.S. Joshi, S.A. Jabarin, D.W. Gidley, M.R. Coleman, Effect of Dimethyl Terephthalate and Dimethyl Isophthalate on the Free Volume and Barrier Properties of Poly(ethylene terephthalate) (PET): Amorphous PET, *Macromolecules*. 51 (2018) 456–467. <https://doi.org/10.1021/acs.macromol.7b02230>.
- [5] K.L. Hoy, Solubility Parameter as a Design Parameter for Water Borne Polymers and Coatings, *Journal of Coated Fabrics*. 19 (1989) 53–67. <https://doi.org/10.1177/152808378901900106>.
- [6] C.M. Hansen, 50 Years with solubility parameters—past and future, *Progress in Organic Coatings*. 51 (2004) 77–84. <https://doi.org/10.1016/j.porgcoat.2004.05.004>.
- [7] B.C. Hancock, P. York, R.C. Rowe, The use of solubility parameters in pharmaceutical dosage form design, *International Journal of Pharmaceutics*. 148 (1997) 1–21. [https://doi.org/10.1016/S0378-5173\(96\)04828-4](https://doi.org/10.1016/S0378-5173(96)04828-4).
- [8] A.N. Ghebremeskel, C. Vemavarapu, M. Lodaya, Use of surfactants as plasticizers in preparing solid dispersions of poorly soluble API: Selection of polymer–surfactant combinations using solubility parameters and testing the processability, *International Journal of Pharmaceutics*. 328 (2007) 119–129. <https://doi.org/10.1016/j.ijpharm.2006.08.010>.

- [9] C.M. Hansen, Hansen solubility parameters: a user's handbook, 2nd ed, CRC Press, Boca Raton, 2007.
- [10] S. Karan, Z. Jiang, A.G. Livingston, Sub-10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation, *Science*. 348 (2015) 1347–1351. <https://doi.org/10.1126/science.aaa5058>.
- [11] W. Kushida, R.R. Gonzales, T. Shintani, A. Matsuoka, K. Nakagawa, T. Yoshioka, H. Matsuyama, Organic solvent mixture separation using fluorine-incorporated thin film composite reverse osmosis membrane, *J. Mater. Chem. A*. 10 (2022) 4146–4156. <https://doi.org/10.1039/D1TA09192A>.
- [12] K.P. Bye, V. Loianno, T.N. Pham, R. Liu, J.S. Riffle, M. Galizia, Pure and mixed fluid sorption and transport in Celazole® polybenzimidazole: Effect of plasticization, *Journal of Membrane Science*. 580 (2019) 235–247. <https://doi.org/10.1016/j.memsci.2019.03.031>.
- [13] C. Andecochea Saiz, S. Darvishmanesh, A. Buekenhoudt, B. Van der Bruggen, Shortcut applications of the Hansen Solubility Parameter for Organic Solvent Nanofiltration, *Journal of Membrane Science*. 546 (2018) 120–127. <https://doi.org/10.1016/j.memsci.2017.10.016>.
- [14] J. da Silva Burgal, L. Peeva, P. Marchetti, A. Livingston, Controlling molecular weight cut-off of PEEK nanofiltration membranes using a drying method, *Journal of Membrane Science*. 493 (2015) 524–538. <https://doi.org/10.1016/j.memsci.2015.07.012>.
- [15] S. Postel, G. Spalding, M. Chirnside, M. Wessling, On negative retentions in organic solvent nanofiltration, *Journal of Membrane Science*. 447 (2013) 57–65. <https://doi.org/10.1016/j.memsci.2013.06.009>.
- [16] S. Venkatram, C. Kim, A. Chandrasekaran, R. Ramprasad, Critical Assessment of the Hildebrand and Hansen Solubility Parameters for Polymers, *J. Chem. Inf. Model*. 59 (2019) 4188–4194. <https://doi.org/10.1021/acs.jcim.9b00656>.
- [17] D.W. van Krevelen, Properties of polymers: their correlation with chemical structure, their numerical estimation and prediction from additive group contributions, 3rd, completely rev. ed ed., Elsevier, Amsterdam ; New York, 1990.
- [18] M.B. Huglin, D.J. Pass, Cohesive energy density of polytetrahydrofuran, *Journal of Applied Polymer Science*. 12 (1968) 473–485. <https://doi.org/10.1002/app.1968.070120308>.
- [19] G. Gee, The interaction between rubber and liquids. III. The swelling of vulcanised rubber in various liquids, *Trans. Faraday Soc.* 38 (1942) 418–422. <https://doi.org/10.1039/TF9423800418>.
- [20] C.H. Mah, Q. Wu, G.R. Deen, Effect of nature of chemical crosslinker on swelling and solubility parameter of a new stimuli-responsive cationic poly(N-acryloyl-N'-propyl piperazine) hydrogel, *Polym. Bull.* 75 (2018) 221–238. <https://doi.org/10.1007/s00289-017-2029-8>.
- [21] C. Kim, A. Chandrasekaran, T.D. Huan, D. Das, R. Ramprasad, Polymer Genome: A Data-Powered Polymer Informatics Platform for Property Predictions, *J. Phys. Chem. C*. 122 (2018) 17575–17585. <https://doi.org/10.1021/acs.jpcc.8b02913>.
- [22] A.X. Wu, S. Lin, K. Mizrahi Rodriguez, F.M. Benedetti, T. Joo, A.F. Grosz, K.R. Storme, N. Roy, D. Syar, Z.P. Smith, Revisiting group contribution theory for estimating fractional free volume of microporous polymer membranes, *Journal of Membrane Science*. 636 (2021) 119526. <https://doi.org/10.1016/j.memsci.2021.119526>.
- [23] M.T. Webb, L.C. Condes, H.G. Ly, M. Galizia, S. Razavi, Rational design, synthesis, and characterization of facilitated transport membranes exhibiting enhanced permeability,

- selectivity and stability, *Journal of Membrane Science*. 685 (2023) 121910. <https://doi.org/10.1016/j.memsci.2023.121910>.
- [24] D. Mangaraj, Cohesive energy densities of high polymers. Part I. Determination of cohesive energy density from swelling measurements, *Die Makromolekulare Chemie*. 65 (1963) 29–38. <https://doi.org/10.1002/macp.1963.020650104>.
- [25] D.J. Kent, R.C. Rowe, Solubility studies on ethyl cellulose used in film coating, *Journal of Pharmacy and Pharmacology*. 30 (1978) 808–810. <https://doi.org/10.1111/j.2042-7158.1978.tb13403.x>.
- [26] P. Franco, I. De Marco, The Use of Poly(N-vinyl pyrrolidone) in the Delivery of Drugs: A Review, *Polymers*. 12 (2020) 1114. <https://doi.org/10.3390/polym12051114>.
- [27] L. Li, Z. Jiang, J. Xu, T. Fang, Predicting poly(vinyl pyrrolidone)'s solubility parameter and systematic investigation of the parameters of electrospinning with response surface methodology, *Journal of Applied Polymer Science*. 131 (2014). <https://doi.org/10.1002/app.40304>.
- [28] K. Nasouri, A.M. Shoushtari, M.R.M. Mojtahedi, Thermodynamic Studies on Polyvinylpyrrolidone Solution Systems Used for Fabrication of Electrospun Nanostructures: Effects of the Solvent, *Advances in Polymer Technology*. 34 (2015). <https://doi.org/10.1002/adv.21495>.
- [29] M.F. Pina, M. Zhao, J.F. Pinto, J.J. Sousa, D.Q.M. Craig, The influence of drug physical state on the dissolution enhancement of solid dispersions prepared via hot-melt extrusion: a case study using olanzapine, *J Pharm Sci*. 103 (2014) 1214–1223. <https://doi.org/10.1002/jps.23894>.
- [30] H. Yin, Y.Z. Chua, B. Yang, C. Schick, W.J. Harrison, P.M. Budd, M. Böhning, A. Schönhals, First Clear-Cut Experimental Evidence of a Glass Transition in a Polymer with Intrinsic Microporosity: PIM-1, *J. Phys. Chem. Lett*. 9 (2018) 2003–2008. <https://doi.org/10.1021/acs.jpclett.8b00422>.
- [31] M. Minelli, K. Friess, O. Vopička, M.G. De Angelis, Modeling gas and vapor sorption in a polymer of intrinsic microporosity (PIM-1), *Fluid Phase Equilibria*. 347 (2013) 35–44. <https://doi.org/10.1016/j.fluid.2013.03.003>.
- [32] A.A. Yushkin, T.S. Anokhina, S.D. Bazhenov, I.L. Borisov, P.M. Budd, A.V. Volkov, Sorption and Nanofiltration Characteristics of PIM-1 Material in Polar and Non-Polar Solvents, *Pet. Chem*. 58 (2018) 1154–1158. <https://doi.org/10.1134/S096554411813011X>.
- [33] S. Thomas, I. Pinnau, N. Du, M.D. Guiver, Pure- and mixed-gas permeation properties of a microporous spirobisindane-based ladder polymer (PIM-1), *Journal of Membrane Science*. 333 (2009) 125–131. <https://doi.org/10.1016/j.memsci.2009.02.003>.
- [34] K. Nagai, T. Masuda, T. Nakagawa, B.D. Freeman, I. Pinnau, Poly[1-(trimethylsilyl)-1-propyne] and related polymers: synthesis, properties and functions, *Progress in Polymer Science*. 26 (2001) 721–798. [https://doi.org/10.1016/S0079-6700\(01\)00008-9](https://doi.org/10.1016/S0079-6700(01)00008-9).
- [35] A. Morisato, B.D. Freeman, I. Pinnau, C.G. Casillas, Pure hydrocarbon sorption properties of poly(1-trimethylsilyl-1-propyne) (PTMSP), poly(1-phenyl-1-propyne) (PPP), and PTMSP/PPP blends, *Journal of Polymer Science Part B: Polymer Physics*. 34 (1996) 1925–1934. [https://doi.org/10.1002/\(SICI\)1099-0488\(199608\)34:11<1925::AID-POLB10>3.0.CO;2-B](https://doi.org/10.1002/(SICI)1099-0488(199608)34:11<1925::AID-POLB10>3.0.CO;2-B).
- [36] K. Hornik, M. Stinchcombe, H. White, Multilayer feedforward networks are universal approximators, *Neural Networks*. 2 (1989) 359–366. [https://doi.org/10.1016/0893-6080\(89\)90020-8](https://doi.org/10.1016/0893-6080(89)90020-8).

- [37] A.F.M. Barton, CRC handbook of polymer-liquid interaction parameters and solubility parameters, CRC Press, Boca Raton, 1990.