Research Article

V. G. Kulichikhin, A.Ya. Malkin*, I.V. Gumennyi, and V.A. Govorov

Rheology of polysulfone-N-methylpyrrolidone solutions used in the technology of lithium-ion batteries

https://doi.org/10.1515/arh-2020-0109
Received Mar 08, 2020; accepted Sep 15, 2020

Abstract: This paper is devoted to the analysis of the rheological properties of polysulfone solutions in N-methylpyrrolidone, which are an intermediate stage in preparing lithium-ionic batteries. The viscosity of the solutions has been measured in wide ranges of shear rate, temperature, and concentration. The crucial role of water in measuring the rheological properties of solutions has been observed and avoided. The solutions under study are Newtonian liquids, but they demonstrate the elasticity at moderately high concentrations. The concentration dependence of viscosity is very strong, and the threshold was found where the viscosity grows unlimitedly due to the transition of the solution to the gel-like state. Temperature dependences of viscosity are described by the Arrhenius-type equation with the activation energy increasing along with an increase in the polymer concentration in solutions.

Keywords: polymers, rheology, polymer solutions, polysulfone, solution-to-gel transition

1 Introduction

Polymers are an important component used in lithium-ionic batteries which are widely used in modern techniques. Among others, polysulfone (PSu in N-methyl-2-pyrrolidone (NMP)) solutions are a promising material in such devices as separators. This is explained by high temperature and chemical stability, as well as the strength of this polymer. Furthermore, PSu is characterized by the perfect transport characteristics and is often used in membrane technique [1, 2]. Its dielectric constant is app. 3.3-3.2, and its sulfonic group is apparently excellent for the Li$^+$ cation solvation [3, 4]. This should provide the optimal interaction between the polymer and cations for ion diffusion.

One of the main areas of application of PSu solutions regarding its use is in the membrane technology. The rheological properties of PSu solutions play a dominant role in determining the quality of final products [5–7], affecting the morphology of membranes and, consequently, their permeability [8, 9], while the presence of additives in the solvent is a very important part in determining the final morphology and purpose of the film, especially for water [10].

The initial stage of the technological process is related to preparing PSu solutions in N-methyl-2-pyrrolidone. This stage is crucial for formation thin films, and therefore the rheological properties of the solutions are important. First of all, the concentration dependencies of viscosity play a central role, although the elasticity of the solutions can be also taken into consideration. It is worth mentioning that the rheology of PSu solutions may differ markedly from numerous experimental data and their generalization for many industrial flexible-chain polymers [11].

Current publications do not offer sufficient information on this point. Therefore, it seems necessary to clear up the situation concerning the rheology of PSu-methyl pyrrolidone solutions. This is the goal of this study.

Some preliminary data concerning these solutions were published in our previous work [12]. Meanwhile, further experimental studies have shown that there is a need to return to this topic and conduct some additional experiments. The main reason is the very high sensitivity of the rheological properties of PSu solutions to the presence of even minor traces of water, which was not previously taken into account. To obtain more reliable results, a special instrumental modification was performed. Then a wider set of experimental methods was used. Thus, this work continues our research on the rheology of this interesting object started in [12].

*Corresponding Author: A.Ya. Malkin: Institute of Petrochemical Synthesis, Russian Academy of Sciences, Russia, 119991, Moscow, 29, Leninskii prospect; Email: alex_malkin@mig.phys.msu.ru
V. G. Kulichikhin, I.V. Gumennyi, V.A. Govorov: Institute of Petrochemical Synthesis, Russian Academy of Sciences, Russia, 119991, Moscow, 29, Leninskii prospect

© 2020 V. G. Kulichikhin et al., published by De Gruyter. This work is licensed under the Creative Commons Attribution 4.0 License
2 Experimental Section

The experiments were performed with solutions containing from 0.1 to 29 vol.% of PSu.

The PSu sample was a commercial product (Trade mark PSF=150) produced by the Institute Plastmassy (Institute of Plastic) (Moscow, Russia).

The chemical structure of PSu is:

![Chemical structure of PSu](image)

This structure was confirmed by the method of IR-spectroscopy using the FTIR-spectrometer IFS-66 v/s (Bruker, Germany), (scan-30, resolution 2 sm$^{-1}$, range 0–4.000 sm$^{-1}$).

The molecular weight (MW) of PSu was measured by the Gel Permeation Chromatography (GPC) method on the modular high-pressure liquid chromatograph with a LabAlliance Series 1500 Constant Flow Pump (Scientific Systems, USA). The Refractive Index Detector 2142 (LKB, Sweden) was used.

Molecular weights were calculated based on polystyrene standards. The treatment of the obtained experimental data shows that the sample under study is characterized by the following parameters: $M_n = 3.2 \cdot 10^4$, $M_w = 5.6 \cdot 10^4$, and $M_w/M_n = 1.73$.

More details concerning the methodological part and characterization of the polymer used can be found in our preliminary work [12].

N-Methyl-2-Pyrrolidone (NMP) is an aprotic, polar solvent. It was supplied by RussChim Co (Russia) and was used without further purification. The content of water is 0.33 wt. %, Boiling point is 202\(^\circ\)C, density 1.03 g/sm$^3$. Its chemical formula is:

![Chemical structure of NMP](image)

The water content in supplied NMP was determined using volumetric Fischer titration. The titrant was weighed using a high-precision scale (error $\pm 0.0002$ g). The water content was 0.1%.

The intrinsic viscosity [$\eta$] of PSu in NMP was measured by the standard method on the Ubbelohde viscometer.

The rheological properties of all solutions were measured using the Kinexus Pro (Malvern Panalytical, GB) rotation rheometer. The measuring cell was placed into an active housing with automatic temperature control realized by the Peltier module allowing for the temperature stabilization with accuracy of 0.01\(^\circ\)C. The cone-plate and plate-plate operating units were used for measuring. The angle between the cone surface and plate was 1\(^\circ\) and the diameter of the cone was 40 mm. In the application of the plate-plate pair, the diameters of the upper and lower plates were 20 and 55 mm, respectively.

Additionally, the coaxial cylinder working unit (volume of a sample 30 mL) was used, with the diameters of the outer and inner cylinder being $d_o = 15.4$ mm and $d_i = 14$ mm, respectively. Flow curves were measured in the range of shear rates of $\dot{\gamma} = 10^{-2} – 10^2$ s$^{-1}$ in the shear rate control mode. Typically, the experiments were performed in a scanning regime with the duration of shearing at each rate of approximately 20 s. However, some experimental points were controlled by shearing for a long time (max 60 s), until reaching the steady regime of the flow.

3 Results and Discussion

Initial observations showed that the rheological properties of PSu-NMP solutions are very sensitive to the presence of water. When conducting experiments with open boundary surfaces of the samples, it is impossible to make accurate measurements, since the apparent viscosity begins to change from the very beginning of the experiment. Therefore, we made an attempt to modify the working node of the device, which is shown in Figure 1. The results of comparison of the modified working unit and the standard one are shown in Figure 2, which shows the dependence of the viscosity of various polysulfone solutions over time.

![Figure 1: A scheme of the measuring unit with protective cups](image)
The modification of the measuring unit was based on the addition of a special protection against contact of the sample (PS solution) with the surrounding atmosphere. This was achieved by adding two layers of protective cups, shown in Figure 1. They create a sandwich structure with a gap between two protective flaps. Then a layer of phosphorus oxide was placed between these dampers for water sorption. This method of measurement made it possible to exclude the contact of the sample with air and the penetration of moisture from the air into the sample.

Indeed, the use of this design allowed us to eliminate the influence of the environment. Using the modification of the device, as described above, we were able to obtain constant (in time) and well reproducible data (as shown in Figure 2). Only these data will be used in further discussion.

This modification is especially important when carrying out experiments to determine the frequency dependence of the viscosity and elasticity moduli, which will be shown below.

According to the experimental data obtained in our previous publication [12] and confirmed in this work, the viscosity of PSu solutions, measured with a shear rate change in range of four orders is constant and therefore all solutions are truly Newtonian liquids. Possibly, this is explained by a rather low MW of the used polymer. Thus, in the further discussions, it is possible to use a single value of the viscosity, not referring it to the shear rate.

The concentration dependence of the viscosity is presented in Figure 3, including the range of dilute solutions. Let us discuss different concentration ranges in more detail.

The initial part of the concentration range allowed us to determine the intrinsic viscosity $[\eta]$ and the Huggins constant. The concentration dependence of the viscosity of dilute solutions gives the value of $[\eta]$ equal to 0.482 dL/g [12].

The standard definition of the concentration range of dilute solutions is $c'[\eta] = 1$, which corresponds to $c'$ of the order of $\varphi = 0.02$. This estimation is correct for spherical coins, and it is reasonable to assume in our case that it is significantly less. According to our experimental data, the concentration of the crossover point is close to 0.05 (as shown by dotted lines). At higher concentrations, the intensive growth of the viscosity begins (Figure 3), and it corresponds to the transition to the concentration range of the semi-dilute solutions though the flow properties remain Newtonian, as was shown in [12].

This growth continues with strong acceleration, and a very sharp increase in viscosity is observed at approaching a threshold value close to $\varphi \approx 0.5$. This can be treated as the limit of solubility and the transition of the PSu-NMP solution to gel-state.

The concentration dependence of the viscosity in the whole concentration range, including the concentration range beyond $\varphi^*$, is well approximated by an exponential function:

$$\eta = \eta_0 e^{K\varphi}$$  \hspace{1cm} (1)

However, if we are to assume that viscosity grows unlimitedly in approaching $\varphi^*$, it appears necessary to use more a complicated empirical equation, which can be written as:

$$\frac{\eta}{\eta_0} = \left(\frac{\varphi^*}{\varphi^* - \varphi}\right)^{1/d}$$  \hspace{1cm} (2)

where the constant $d = 0.09$.

This equation is presented by the curve in Figure 3.

Temperature dependencies of the solution viscosity are presented in Figure 4 and Figure 5 in the linear and Arrhenius coordinates, respectively.
Temperature dependencies of the viscosity for PSu-NMP solution are quite well fitted by the Arrhenius equation for the temperature activated processes:

\[ \eta = e^{E/RT} \]  

Activation energy \( E \), increases along with the increasing concentration, being equal to 20.1, 24.3, 26.1, and 28.4 J/mol for concentrations \( \varphi \) equal to 9, 13, 15, and 17 vol.\%, respectively.

PSu solutions are Newtonian liquids. However, they demonstrate elastic behavior that is seen from the existence of the frequency dependencies of the storage modulus, as presented in Figure 6. These experimental results are close to ones obtained for PSu solutions used in the preparing membranes [5]. In the range of dilute solutions, the elasticity is not detected. However, above the concentration of app. 15 vol.\%, the frequency dependencies of the storage modulus become quite measurable. Moreover, the experimental data illustrate the continuous transition from semi-concentrated solution (15 vol.\%) with a slope of 2.0 to the typical viscoelastic liquids with a wide relaxation spectrum that is reflected by the decrease in the slope from 2.0 to 1.52. Actually, this is not exact as shown in Figure 6. Comparing Figure 6 with Figure 11 from ref. [12], it can be seen that the use of a modified measuring unit makes it possible to establish that the frequency dependence of the elastic modulus \( G'(\omega) \) does not have a single-relaxation time, as was previously assumed. It is also clearly seen that in an isolated measurement system, the slope of the elastic modulus curves differs from the angle in a non-isolated system.

Frequency dependencies of the loss modulus are uninteresting. They are linear functions of frequency that correspond to the Newtonian behavior of these solutions in the steady flow (Figure 3).

Therefore, we encounter the rather interesting case of Newtonian liquids demonstrating elasticity. In the frequency range under study, \( G'' \gg G' \). Meanwhile the slope of the \( G'(\omega) \) dependencies is always higher than the slope of the \( G''(\omega) \) dependencies. Then, one can expect that the crossover of these curves exists, but it happens at very high frequencies much beyond the window of this study.

4 Conclusion

Detailed examination of the rheological properties of PSu solutions in MNP used in the technology of lithium-ionic batteries has been carried out. Special attention in performing experiments was paid on excluding water sorption by the solvent that can distort experimental data. The solution under study are Newtonian liquids in a wide concentration range, although moderately concentrated solutions demonstrate elastic properties. The viscosity grows rather abruptly with an increase in polymer concentra-
tion, and the threshold of the solution-to-gel-like state is reached at the polymer concentration of the order of 0.5. The temperature dependence of the viscosity of solutions is well fitted by the Arrhenius law, with the activation energy increasing along with an increase in concentration.

Acknowledgement: This work was supported by the Russian Science Foundation grant (Agreement 17-79-30108).

References

[1] Dong X, Ai-Jumali A, Escobar IC. Investigation of the Use of a BI-Derived Solvent for Non-Solvent-Induced Phase Separation (NIPS) Fabrication of Polysulfone Membranes. Membranes. 2018; 8: 1 – 17. doi: 10.3390/membranes8020023
[2] Rozuki NFA, Tajuddin MH, Yusof N. Effect of different solvent on asymmetric polysulfone (PSF) membranes for CO$_2$/CH$_4$ separation. Environment & Ecosystem Science. 2018; 2: 11 – 14 (2018). doi: 10.26480/ees.02.2018.11.14
[3] Baker RW. Membrane Technology and Applications. 3rd ed. Wiley: Hoboken; NJ; 2012.
[4] Harry KJ. Lithium dendrite growth through solid polymer electrolyte membranes. UC Berkeley Electronic Theses and Dissertations. 2016; 1 – 125. doi: 10.2172/1481923
[5] Mousavi SM, Zadhoush A. Investigation of the relation between viscoelastic properties of polysulfone solutions, phase inversion process and membrane morphology: The effect of solvent power. Journal of Membrane Science. 2017; 532: 47–57. doi: 10.1016/j.memsci.2017.03.006
[6] Jansen JC, Macchione M, Oliviero C, Mendichi R, Ranieri GA, Drioli E. Rheological evaluation of the influence of polymer concentration and molar mass distribution on the formation and performance of asymmetric gas separation membranes prepared by dry phase inversion. Polymer, 2005; 46(25): 11366–11379. doi: 10.1016/j.polymer.2005.10.041
[7] Ismail A, Lai P. Effects of phase inversion and rheological factors on formation of defect-free and ultrathin-skinned asymmetric polysulfone membranes for gas separation. Separation and Puriﬁcation Technology. 2003; 33(2): 127-143. doi: 10.1016/s1383-5866(02)00201-0
[8] Shahmirzadi AMA, Hosseini SS, Ruan G, Tan NR. Tailoring PES nanofiltration membranes through systematic investigations of prominent design, fabrication and operational parameters. RSC Advances. 2015; 5(61): 49080–49097. doi: 10.1039/c5ra05985b
[9] Wang L, Li Z, Ren J, Li S-G, Jiang C: Preliminary studies on the gelation time of poly(ether sulfones) membrane-forming system with an elongation method. Journal of Membrane Science. 2016; 275(1-2): 46–51. doi: 10.1016/j.memsci.2005.08.019
[10] Appaw C, Gilbert RD, Khan SA, Kadla JF. Viscoelastic Behavior of Cellulose Acetate in a Mixed Solvent System. Biomacromolecules. 2007; 8(5): 1541–1547. doi: 10.1021/bm0611681
[11] Malkin AYa, Isayev YaA. Rheology. Concepts, methods, Applications. 3rd ed. Chemtec, Toronto; 2018.
[12] Shambilova GK, Pavlyuchkova EA, Govorov VA, Gumennyi IV, Taltenev AA, Malkin AYa. Rheology of Polysulfone and Its Solutions. Polymer Science. 2019; Series A, 61(2): 208-214. doi: 10.1134/S0965545X19020111
[13] Kuhn W, Kuhn H. Die Abhängigkeit der Viskosität vom Strömungsfläche bei hochverdünnten Suspensionen und Lösungen. Helvetica Chimica Acta. 1945; 28: 97-127. doi: 10.1002/hlca.19450280111