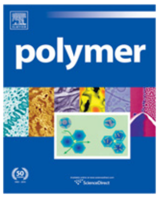
Polymer 51 (2010) 1882–1886

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Polymer Communication

Rheological analysis of oligomeric perfluoropolyethers

Myung S. Jhon[a,b], Hyoung Jin Choi[c,*]

[a] Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA
[b] School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Republic of Korea
[c] Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

A R T I C L E I N F O

Article history:
Received 18 August 2009
Received in revised form
8 February 2010
Accepted 25 February 2010
Available online 6 March 2010

Keywords:
PFPE
Rheology
End group functionality

A B S T R A C T

The novelty lies on the molecular level investigation of the end group functionality on rheological properties of fractionated, monodisperse oligomeric perfluoropolyethers (PFPEs) with various molecular weights and chain-end functionalities in this study. A sharp transition observed in the slope of the shear viscosity at a critical molecular weight for PFPEs was interpreted based on temporal tube mechanism caused by end group agglomeration of strong functional polar end groups. The temperature dependence of the shear viscosity was found to yield an Arrhenius form, determining the flow activation energy and hydrodynamic volume. The flow activation energy was also compared to the activation energy for surface diffusion to examine the role of end group–solid surface interaction. Modified Cole–Cole plots for storage and loss moduli along with polymer relaxation show the microstructural changes due to the interaction of PFPE end-group, which alters effective molecular weights.

1. Introduction

Rheological characteristics of the perfluoropolyethers (PFPEs) have been studied both experimentally [1–10] and numerically [11–13], because of their industrial importance in current information storage devices via their various carbon overcoats for hard disk drives' reliability and lubrication, and interesting relationship between their tribological characteristics and rheological properties. Kono et al. [3] measured shear viscosity and dynamic moduli for fractionated PFPEs with different molecular weights and end group functionalities reporting the existence of the critical molecular weight. Jiang et al. [11] studied viscosity and relaxation time of the four short-chain PFPEs with varied architectural modifications using non-equilibrium molecular dynamics simulation. Furthermore, the surface diffusion coefficient, measured by scanning microellipsometry (SME), was also correlated with shear viscosity [14] to investigate the replenishment, spin-off, and retention of PFPEs [15]. In addition to PFPE bulk rheology, the solution rheology was also investigated. During the manufacturing dip-coating process, the intrinsic viscosity for dilute PFPE solutions was measured to examine the solvent effect for dispersion quality [16]. Shape effect of PFPE molecules in solvents or strongly interacting particles in suspension, interaction among the particles, agglomerations at low concentration, and the formation of the flocs were correlated with solution viscosity, in which the apparent shape of the PFPE is more “non-spherical,” suggesting a larger amount of cluster formations. These cluster formations in the solution (or changes in aspect ratio) are related to the dispersion quality of the PFPEs and may result in undesirable product during the manufacturing processes. Nonetheless, its complete physical understanding and the underlying rheological response for the polymers (oligomers) with reactive end group remain challenging problem despite considerable research on PFPE as a hard disk drive (HDD) lubricant.

In this communication, we focus on molecular rheological analysis of fractionated, monodisperse PFPEs with different molecular weights and end group functionalities (PFPE Z and Zdol with different O/C end group ratios). Although our focus is primarily on temperature and end group functionality effect in bulk rheology, and less on confined geometric effects, our finding will provide insight towards nanorheological responses where polymers (or oligomers) with polar end groups are confined in nano spacing or making nano films. Therefore, our findings reported here can be useful in providing the molecular design criteria such as nano lubricants used in the information storage devices.

2. Experimental part

The PFPEs examined here are from the class of commercially available perfluoropolymeric liquids (Montefluos Co., Milan, Italy) [17] under the trade name Fomblin Z, which were obtained from tetrafluoroethylene via the direct photooxidation and the

---

[*] Corresponding author. Tel.: +82 32 860 7486; fax: +82 32 865 5178.
E-mail address: hjchoi@inha.ac.kr (H.J. Choi).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.02.044

successive thermal treatment and neutralization so as to allow different compositions of oxydifluoromethylene and oxytetrafluoroethylene units [18]. Their base molecular structure is comprised of carbon, fluorine, and oxygen with a linear chain. The perfluoroalkylenic units are linked by means of an oxygen atom. They are potentially suitable lubricants under arduous conditions and in the presence of chemicals and oxidizing reagents.

Here, we examined the rheological response of monodisperse, difunctional derivatives of Fomblin Z (i.e., Zdol and ZdolTX [3]), which are random copolymers with the following linear backbone chain structure:

$$X - CF_2 - \left[(OCF_2CF_2)_m - (OCF_2)_n\right] - OCF_2 - X \quad (m/n = 2/3).$$

Here, the end group Xs for Z, Zdol, and ZdolTX are: $X = CF_3$, $X = CH_2{-}OH$, and $X = CH_2(OCH_2CH_2)_pOH$ (average $p = 1.5$), respectively.

Note that Zdol has hydroxyl groups at both chain ends that exhibit strong interactions among end group themselves as well as with solid surfaces. Some characteristic physiochemical properties of PFPE Z, Zdol, and ZdolTX are given in Table 1. Number average molecular weights (M_n) and end group functionalities of the Fomblin Z samples were measured by nuclear magnetic resonance, while weight average molecular weights (M_w) were measured by gel permeation chromatography. Polydispersity index ($PI \equiv M_w/M_n$) varied from 1.01 to 1.06, indicating that the PFPEs used are almost monodisperse.

The rheological properties of the PFPEs, including the melt viscosity (μ), storage modulus (G'), and loss modulus (G'') were measured at several different temperatures via steady shear and dynamic oscillatory tests, using a rotational rheometer (Physica LS-100, Germany) with a double gap Couette type cylinder and an air bearing supported measuring device under controlled stress conditions. Since this rheometer has a limited torque range of 10^{-6}–10^{-2} N m and shear rate range of 10^{-6}–10^{3} s^{-1}, we also used a rotational rheometer (Physica MC-120, Germany) with a double gap Couette cell to measure the shear viscosity at higher shear rates ($\sim 10^5$ s^{-1}) [19,20]. Before measuring oscillatory responses, G' and G'', we performed an amplitude sweep test to verify the linear viscoelastic range.

3. Results and discussion

Melt viscosities for different PFPEs were measured as a function of shear rate at various temperatures from the flow curve of shear stress vs. shear rate obtained from the steady shear experiment using a rotational rheometer. The melt viscosities for all PFPEs examined in this paper exhibit Newtonian behavior up to relatively high shear rates of 10^3 s^{-1} and decrease with increasing temperature as shown in the Fig. 1. Similar behavior has been also reported for PFPE Z8 [6]. However, it can be noted that both FomblinZ [21] and Fomblin YR [8] were found to show non-Newtonian behavior at shear rates above 10^4 s^{-1}. Via molecular dynamics simulations, non-Newtonian behaviors at very high shear rates were also demonstrated [11–13,22,23].

Table 1
Physiochemical properties of PFPE Z, Zdol, and ZdolTX.

Material code	M_n	M_w	End group O/C ratio	Terminal relaxation time × 10^5 (sec)
Z8	8000		0	3.86
Zdol1	2000	2745	1	1.82
Zdol2	5422	5558	1	2.70
ZdolTX6	2555	2594	0.7	5.79
ZdolTX8	3547	3675	0.7	4.75
ZdolTX9	4391	4472	0.7	7.65
ZdolTX10	6281		0.7	11.28

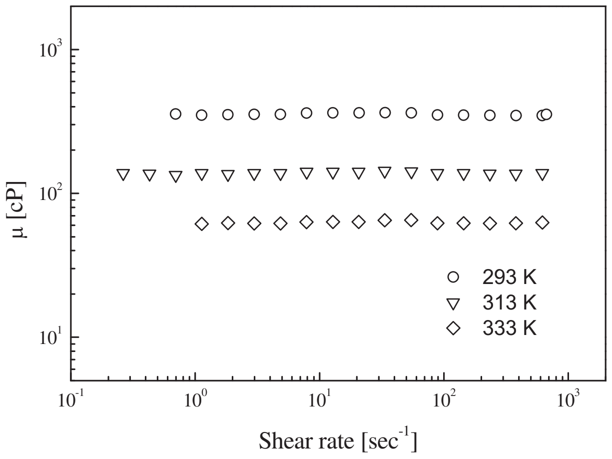


Fig. 1. Shear viscosity *vs.* shear rate for ZdolTX8 at three different temperatures (○: 293 K, ▽: 313 K, and □: 333 K).

From the temperature dependence of shear viscosity, which yields an Arrhenius form, the flow activation energy E_μ^* and the hydrodynamic volume $\mu_0 = N_A h/V$ (N_A is Avogadro's number, h is Planck constant, and V is the molar volume) were determined:

$$\mu = \mu_0 \exp\left(E_\mu^*/RT\right) \text{ or } \ln\mu = \ln\mu_0 + E_\mu^*/RT \tag{1}$$

where R is the gas constant and T is absolute temperature. When $\ln\mu$ is plotted against $1/T$, which yields straight lines with a positive slope, increasing slightly with molecular weight for PFPE Z, Zdol, and ZdolTX [3,6,14]. E_μ^* increases with both molecular weight and increasing O/C ratio in the end groups. The activation energy for PFPE Z is lower than those of Zdol or ZdolTX implying that E_μ^* depends strongly on the interaction strength of functional end group, and less on the actual molecular weight (M).

However, our experimental data exhibits the peculiar melt viscosity, which is strongly dependent on M via end group coupling. This remarkable observation is: if M is less than a critical molecular weight M_C , the melt viscosity increases linearly with M or $M^{0.5}$. However, when M is greater than M_C, the melt viscosity increases much more rapidly with M.

It is well-known that high molecular weight, monodisperse, linear polymer melts follow [24]:

$$\begin{aligned} &\mu \propto M \text{ or } M^{0.5} \text{ for } M < M_C \\ &\text{and } \mu \propto M^{3.4} \text{ for } M > M_C \end{aligned} \tag{2}$$

Here, the critical molecular weight M_C has been interpreted as the molecular weight at which entanglement coupling occurs [25]. De Gennes introduced the “reptation” model for tagged polymer molecules in polymeric melt systems [24], stating that the polymer motion is much like that of a snake moving in the contorted “tunnel” formed by the surrounding polymer molecules, and interpreted $\mu \propto M^3$ behavior for $M > M_C$. We found similar phenomena for low molecular weight PFPE with very strong end group functionality as shown below.

For PFPE systems, as shown in Fig. 2, we found that $\mu \propto M^{0.5}$ for all values of M (for Zdol), whereas $\mu \propto M$ for $M < M_C$ and $\mu \propto M^2$ for $M > M_C$ (for ZdolTX) [3]. An M_C on the order of 3600 g/mol was observed for ZdolTX. The melt viscosity was found to increase with increasing end group C/O ratio. Note that Ajrodi et al. [26] observed that the iso-free volume viscosities of Zdol were linearly

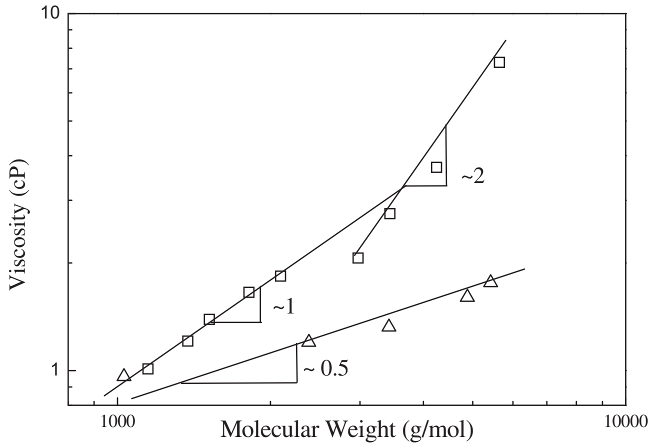


Fig. 2. Shear viscosity of PFPE Zdol and ZdolTX as a function of molecular weight (□: ZdolTX, △: Zdol) [3].

proportional to M above their glass transition temperatures. In contrast, we observed a crossover behavior for ZdolTX possessing bulky end groups. Crossover behavior has been reported for the molecular weight dependence on shear viscosity of PFPEs with bulky end groups [27,28]. Marchionni et al. [27] reported that for various Fomblin Z with different m/n values, the exponent changes from 1.5 to about 2.5, *i.e.*, a value still much below 3.4, which is the typical value for the majority of polymer melts above the critical molecular weight.

The existence of an M_C in ZdolTX data is originated from end group agglomeration, which gives analogous phenomenon to the reptation process. This pseudo-reptation process may arise from strong end group interactions through the formation of a “temporal tube”-like confinement. An illustration of this proposed scenario is given in Fig. 3. The origin of M_C and M^2 dependencies in shear viscosity is very subtle, requiring further investigation.

As end group interaction gets stronger, a higher degree of ordered structure for end groups or agglomerations of end groups appear and exhibit the critical molecular weight, M_C. This suggests that the molecular weight dependence on transport coefficients (*e.g.*, shear viscosity) can be strongly dependent on the strength of end group interaction and temperature.

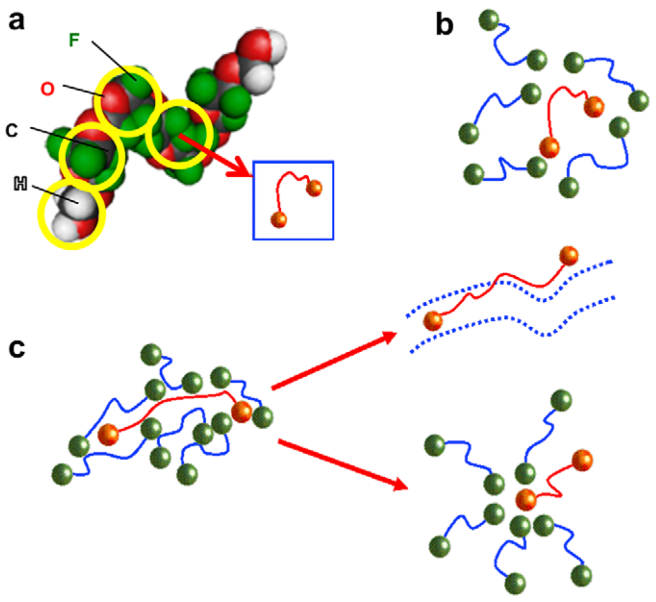


Fig. 3. (a) Simple representation of a PFPE molecule. (b) and (c): Illustration of “temporal tube”-like confinement and agglomerations. Relaxation processes and tube leakage of tagged PFPE molecules for (b) $M < M_c$ and (c) $M > M_c$.

Melt viscosity dependence on temperature was compared with SME measurements [14,15,29–34]. The activation energy for surface diffusion E_d^* (calculated from the SME data using the Arrhenius equation $D = D_0\exp(-E_d^*/RT)$) was compared to the E_μ^*.

$$D\mu^{E_d^*/E_\mu^*} = D_0\exp\left(-E_d^*/RT\right)\left[\mu_0\exp(E_\mu^*/RT)\right]^{E_d^*/E_\mu^*} = D_0\mu_0^{E_d^*/E_\mu^*}. \quad (3)$$

From Eq. (3), it appears that $D\mu^\nu \cong$ constant (or a weak function of temperature), where $\nu = E_d^*/E_\mu^*$ depends on the PFPE–solid surface interaction via end group functionality.

We observed that $\nu \cong 1$ for PFPE Z (Einstein relationship), while $\nu \cong 1.5$ for PFPE Zdol [14], indicating that the mobility of the non-functional PFPE Z does not appear to be influenced by the solid substrate, whereas the Zdol exhibits lower mobility which suggests an additional energy barrier contribution due to polymer–substrate interaction. It is interesting to note that the interaction strength between PFPE end group and solid surface can be estimated via the activation energy ratio (the temperature dependent relationship between D and μ). Note that understanding the spreading of thin films of liquid polymer on solid surfaces by either migration or diffusion of polymers impacts many areas of modern technology, including lubrication of the HDD.

To examine these temporal tube formation or agglomeration of PFPEs due to polar end groups, we conducted oscillatory measurements at different temperatures. Fig. 4 shows the 3-dimensional plot of G'–G''–ω for Zdol1 measured at 303 K. For various PFPEs, we found that the G'' is strongly dependent on temperature, while G' is weakly dependent on temperature [6].

From this oscillatory data, we can estimate the relaxation times (τ_ps) of PFPEs. For example, the Rouse theory [26] for G' and G'' are given by:

$$G' = G_0\sum\frac{(\omega\tau_p)^2}{1+(\omega\tau_p)^2}, \quad (4a)$$

and

$$G'' = G_0\sum\frac{\omega\tau_p}{1+(\omega\tau_p)^2}, \quad (4b)$$

with

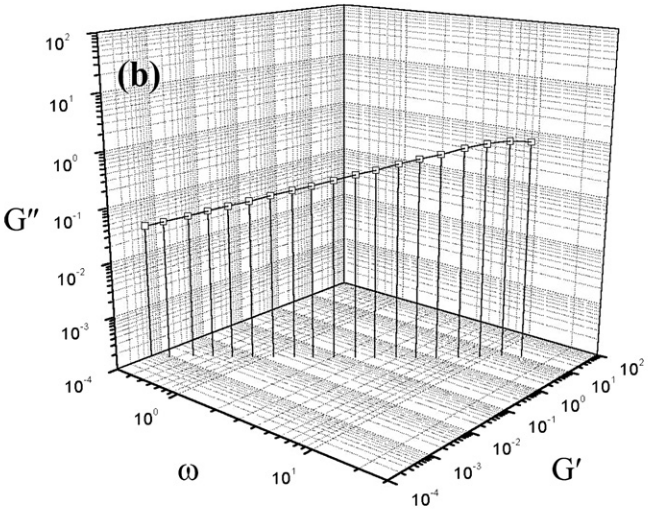


Fig. 4. G'–G''–ω plot for Zdol1 at 303 K.

$$G_0 \equiv \rho RT/M, \tag{4c}$$

where ρ is the specific gravity and ω is the angular frequency. The rheological properties are related to the longest relaxation time $\tau_1 \equiv \tau_p(p = 1)$,

$$\tau_l = \frac{6\mu_0 M}{\pi^2 \rho RT}. \tag{5}$$

τ_l depends on M (chain length) and strongly depends on end group functionality via interaction with either other end groups or solid surface. In Table 1, we summarized the end group effects on τ_1 at 20 °C (see Eq. (5)) in addition to the physiochemical properties of PFPE Z, Zdol, and ZdolTX. The relaxation times of Zdol are slightly smaller than of Z, while those of ZdolTX are much larger than those of Z.

On the other hand, based on the oscillatory measurements of Zdol1 at three different temperature, Fig. 5 shows a modified Cole–Cole plot [35] (G' vs. G'' plot, correlation between the elastic and viscous properties), exhibiting significant sensitivity to variations in temperature. Because all PFPE data in the modified Cole–Cole plot do not collapse onto a single line, we believe the microstructures in the PFPE samples are strongly dependent on temperature. Although our findings are all based on the bulk rheology, we expect a similar trend to be observed in the nanorheology (rheological response in molecular film).

In order to examine its temperature dependence in details, we propose a following simple scaling argument for the dynamic moduli. We can easily find that the Rouse theory in Eq. (4) (set $p = 1$) suggests that

$$G'_R \equiv G'/G_0 = \mathcal{F}_1(\omega\tau_1, \pi), \tag{6a}$$

and

$$G''_R \equiv G''/G_0 = \mathcal{F}_2(\omega\tau_1, \pi) \tag{6b}$$

Here, π is the property containing the end group information and may be strongly dependent on temperature.

By eliminating $\omega\tau_1$ from Eq. (4), we obtain

$$G'_R = \mathcal{F}_1(\omega\tau_1, \pi) = \mathcal{F}\left(\mathcal{F}_2^{-1}(G''_R, \pi)\right) = \mathcal{F}(G''_R, \pi) \tag{7}$$

Here, $\mathcal{F}_1, \mathcal{F}_2,$ and $\mathcal{F}$ are arbitrary functions. Eq. (7) implies that the relationship between G'_R and G''_R depends on temperature via π. Therefore, the G'–G'' plot depends on temperature due to end group functionalities. As a result, strong temperature dependence is observed for the G'–G'' plot (Fig. 5). As it has been studied via molecular dynamics simulation [36], dynamic moduli is strongly dependent on temperature indicating that microstructure especially in the case of functional PFPEs with the strong functional end group coupling occurs.

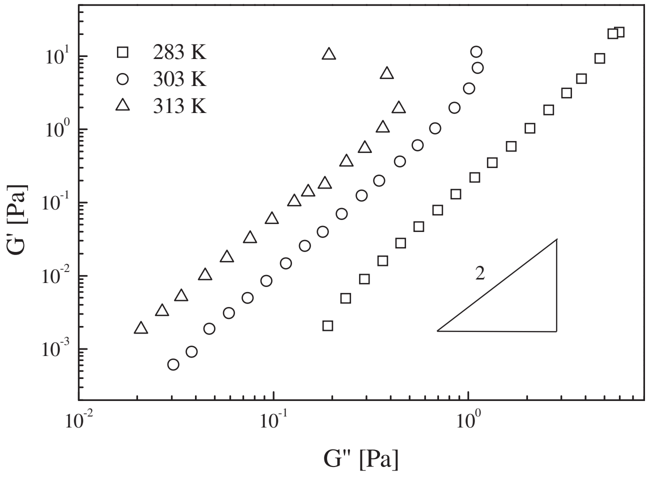


Fig. 5. Modified Cole–Cole plot for PFPE Zdol1.

4. Conclusion

The focus of this communication is on the PFPE system having polar end groups, where the melt viscosity values have shown Newtonian behavior and was found to increase with an increasing end group O/C ratio end group agglomerations/temporal tube formation, and temperature dependence was examined via the Arrhenius equation. The flow activation energy depends weakly on chain length, while strongly depends on chain-end functionality. We have modified Cole–Cole plot, which revealed microstructures from the interaction among the end groups in the bulk PFPE system. Our observation is in agreement with the modified Cole–Cole plot. Loss modulus is strongly dependent on temperature, while storage modulus is weakly dependent on temperature. The characteristic time for Zdol (an end group O/C ratio of 1) was calculated as five times greater than that of ZdolTX (an end group O/C ratio of 0.7). Melt viscosity for ZdolTX is proportional to M^2 above a critical molecular weight. To investigate the role of end group interaction with solid surface, we also examined the relationship between surface diffusion and bulk viscosity.

Acknowledgements

This research was supported, in part, by the National Science Foundation under grant INT-9910429. HJC also appreciates the research fund (39704-1) from National Research Foundation of Korea (2009).

References

[1] Jonsson U, Bhushan B. J Appl Phys 1995;78:3107–14.
[2] Nakamura Y, Kurosaki Y. Microsyst Technol 2005;11:1127–31.
[3] Kono RN, Jhon MS, Choi HJ, Kim CA. IEEE Trans Magn 1999;35:2388–90.
[4] Kono RN, Izumisawa S, Jhon MS, Kim CA, Choi HJ. IEEE Trans Magn 2001;37:1827–9.
[5] Mriziq KS, Dai HJ, Dadmun MD, Jellison GE, Cochran HD. Rev Sci Instrum 2004;75:2171–6.
[6] Choi HJ, Lim ST, Izumisawa S, Jhon MS. Tribol Int 2005;38:682–6.
[7] Choi J, Kato T. Langmuir 2003;19:7933–40.
[8] Mriziq KS, Cochran HD, Dadmun MD. Rheol Acta 2007;46:839–45.
[9] Ohno N, Rahman MZ, Yamada S, Komiya H. Tribol Trans 2009;52:492–500.
[10] Zhang B, Chiba H, Nakajima A. Tribol Lett 2009;35:25–30.
[11] Jiang B, Crawford NJ, Keffer DJ, Edwards BJ, Adcock JL. Molecular Simul 2007;33:871–8.
[12] Choi HJ, Guo Q, Chung PS, Jhon MS. IEEE Trans Magn 2007;43:903–5.
[13] Jiang B, Keffer DJ, Edwards BJ. J Fluorine Chem 2006;127:787–95.
[14] O'Conner TM, Jhon MS, Bauer CL, Min BG, Yoon DY, Karis TE. Trib Lett 1995;1:219–23.
[15] Ma X, Gui J, Grannen KJ, Smoliar LA, Marchon B, Jhon MS, et al. Trib Lett 1999; 6:9–14.
[16] Jhon MS, Izumisawa S, Choi HJ. J Ind Eng Chem 2003;9:508–12.
[17] Ausimont, http://www.ausimont.com/docs/fom_thin.html.
[18] Izumisawa S, Jhon MS. Trib Lett 2002;12:75–81.
[19] Jhon MS, Choi HJ. J Ind Eng Chem 2001;7:263–75.
[20] Jhon MS. Adv Chem Phys 2004;129:1–70.
[21] Cantow MJR, Ting TY, Barrall EM, Porter RS, George ER. Rheol Acta 1986; 25:69–71.
[22] Guo Q, Chung PS, Chen H, Jhon MS. J Appl Phys 2006;99. Art no. 08N105.
[23] Guo Q, Chung PS, Jhon MS, Choi HJ. Macromol Theory Simul 2008;17:454–9.
[24] De Gennes PG. Scaling concepts in polymer physics. Ithaca, NY: Cornell University; 1979.
[25] Bird RB, Curtiss CF, Armstrong RC, Hassager O. Dynamics of polymeric liquids. New York, NY: John Wiley & Sons; 1987.
[26] Ajrodi G, Marchionni G, Pezzin G. Polymer 1999;40:4163–4.
[27] Marchionni G, Ajroldi G, Cinquina P, Tampellini E, Pezzin G. Polym Eng Sci 1990;30:829–34.

[28] Sianesi D, Zamboni V, Fontanelli R, Binaghi M. Wear 1971;18:85–100.
[29] Min BG, Choi JW, Brown HR, Yoon DY, O'Connor TM, Jhon MS. Trib Lett 1995;1:225–32.
[30] O'Connor TM, Back YR, Jhon MS, Min BG, Yoon DY, Karis TE. J Appl Phys 1996;79:5788–90.
[31] Ma X, Gui J, Smoliar L, Grannen K, Marchon B, Bauer CL, et al. Phys Rev E 1999;59:722–7.
[32] Ma X, Gui J, Smoliar L, Grannen K, Marchon B, Jhon MS, et al. J Chem Phys 1999;110:3129–37.
[33] Ma X, Gui J, Marchon B, Jhon MS, Bauer CL. IEEE Trans Magn 1999;35:2454–6.
[34] Ma X, Bauer CL, Jhon MS, Gui J, Marchon B. Phys Rev E 1999;60:5795–801.
[35] Park BJ, Kim TH, Choi HJ, Lee JH. J Macromol Sci B: Phys 2007;46:341–54.
[36] Guo Q, Jhon MS. IEEE Trans Magn 2006;42:2540–2.