

## Surface Diffusion of Polymer Glasses Redux

K. L. Ngai<sup>1</sup>, Simone Capaccioli<sup>1,2</sup>

<sup>1</sup> *CNR-IPCF, Largo B. Pontecorvo 3, I-56127, Pisa, Italy*

<sup>2</sup> *Dipartimento di Fisica, Università di Pisa, Largo B. Pontecorvo 3, I-56127, Pisa, Italy*

### Abstract

Zhang and Yu (Zhang, W.; Yu, L. Surface Diffusion of Polymer Glasses, *Macromolecules* **2016**, *49*, 731–735.) reported the first measurement of surface diffusivity for low molecular weight polystyrene (PS) glasses. They found the enhancement of polymer surface diffusivity is much less compared to small molecule glasses, and correctly identified the penetration of polymer chains into the interior and a steep mobility gradient away from the surface are important factors for the cause. In this Note we point out yet another factor entering the consideration of surface diffusion of PS. Unlike small molecular glass-formers, PS diffusion is carried out by the polymer chain mode, which has dynamics very different from the structural  $\alpha$ -relaxation as evidenced by the breakdown of thermorheological simplicity in bulk PS. Enhancement of surface diffusion of PS chain mode becomes a new problem, which has to be considered in conjunction with the penetration of polymer chains into the interior for a full explanation of the experimental data. Attempt is made to address this problem in part by use of the Coupling Model.

Measurements of the surface self-diffusion coefficients of glass-forming small molecules, indomethacin (IMC)<sup>1</sup>, nifedipine (NIF)<sup>2</sup> and *o*-terphenyl (OTP)<sup>3</sup> by Yu and coworkers using

the method of surface grating decay have found exceedingly large enhancement of molecular mobility at the surface. The decay of surface grating in all three molecules occurs by viscous flow at high temperatures, but by surface diffusion at lower temperatures starting at about ten degrees above  $T_g$ . Surface diffusion coefficient  $D_S$  is  $10^6$  and  $10^8$  times larger than bulk diffusion coefficient  $D_V$  at  $T_g$  in IMC and OTP respectively, and even larger at lower temperatures in the glassy state. Such spectacular findings have attracted quantitative explanations by the Random First Order Transition (RFOT) theory<sup>4</sup>, and the Coupling Model (CM)<sup>5</sup>, both are based on the reduction of the structural  $\alpha$ -relaxation time at the surface from that of the bulk material. These two attempts<sup>4,5</sup> consider the diffusion of IMC and OTP observed by the surface grating decay technique<sup>1,3</sup> are all at the surface with a single surface diffusion constant, and possible spatial mobility gradient of the  $\alpha$ -relaxation and diffusion is ignored. There is also the Elastically Collective Nonlinear Langevin Equation (ECNLE) theory for the  $\alpha$ -relaxation of free-standing polymer films with a spatial mobility gradient and friction of the  $\alpha$ -relaxation averaged within some depth beneath the free surface to account for the penetration of a chain into the bulk.<sup>6,7</sup> The results are in accord with the available experimental data. Parenthetically, the dependence of the mobility of the  $\alpha$ -relaxation on distance from the free surface of polymer thin films also was considered by the CM and accounted for by depth dependent coupling parameter.<sup>8</sup>

In a recently published paper<sup>9</sup>, Zhang and Yu (ZY) reported the first measurement of surface diffusivity for low molecular weight polystyrene (PS) glasses. The results at  $T_g$  show a 5 orders of magnitude enhancement of diffusion at the free surface, much weaker than that for small-molecule glasses, especially OTP. The difference is convincingly attributed by ZY to a

steep mobility gradient away from the surface and deeper penetration of polymer chains into the interior compared to small-molecule glasses.

In this Note we point out another factor entering the consideration of diffusion of low molecular weight PS at the free surface not present in the case of small-molecular glass-formers. For the PS with low molecular weights of 1.1 and 1.7 kg/mol studied by ZY<sup>9</sup>, chain diffusion is carried out by the chain diffusion mode, which in the bulk has dynamics very different from the structural  $\alpha$ -relaxation. The difference is evidenced by the breakdown of thermorheological simplicity, manifested by the viscosity  $\eta$ , chain relaxation time  $\tau_c$ , and chain diffusion coefficient  $D_c$  all having different temperature dependence than that of the structural  $\alpha$ -relaxation time  $\tau_\alpha$ .<sup>10-15</sup> For low molecular weight (MW) PS such as those studied by ZY, the large decrease of the plateau or steady state compliance,  $J_s$ , with decreasing temperature towards  $T_g$  is another manifestation of thermorheological complexity.<sup>10,11,16-19</sup>

Clearly the enhancement of diffusion observed at the free surface of the low MW PS by surface grating decay originated from the PS chain mode and not the structural  $\alpha$ -relaxation. Since the dynamics of PS chain mode are so different from the structural  $\alpha$ -relaxation, the existing explanations<sup>4-7</sup> of enhanced surface mobility for small molecule glasses all based on  $\tau_\alpha$  no longer apply. A new approach based on the chain diffusion mode of the low MW PS, but not the structural  $\alpha$ -relaxation, is needed to fully understand the size of the enhancement of its surface diffusion. In addition, the effect of the chain mobility gradient and the penetration of polymer chains into the interior has to be included as emphasized by ZY<sup>9</sup>. The enhancement of PS chain surface diffusion coefficient measured by surface grating decay method becomes a novel and interesting problem. Thus the study by ZY<sup>9</sup> of PS brings into the field another new perspective. This one is the intriguing connection

of the polymer surface diffusion data to chain dynamics and thermorheological complexity in viscoelasticity of bulk polymers.

In substantiating the points made above, we collected the data of the viscosity,  $\eta$ ,<sup>20</sup> the recoverable compliance,  $J_s$ , and the  $\alpha$ -relaxation time,  $\tau_\alpha$ , of PS with MW=2 kg/mol (PS2K)<sup>15</sup> and plotted them against reciprocal temperature in Fig.1.

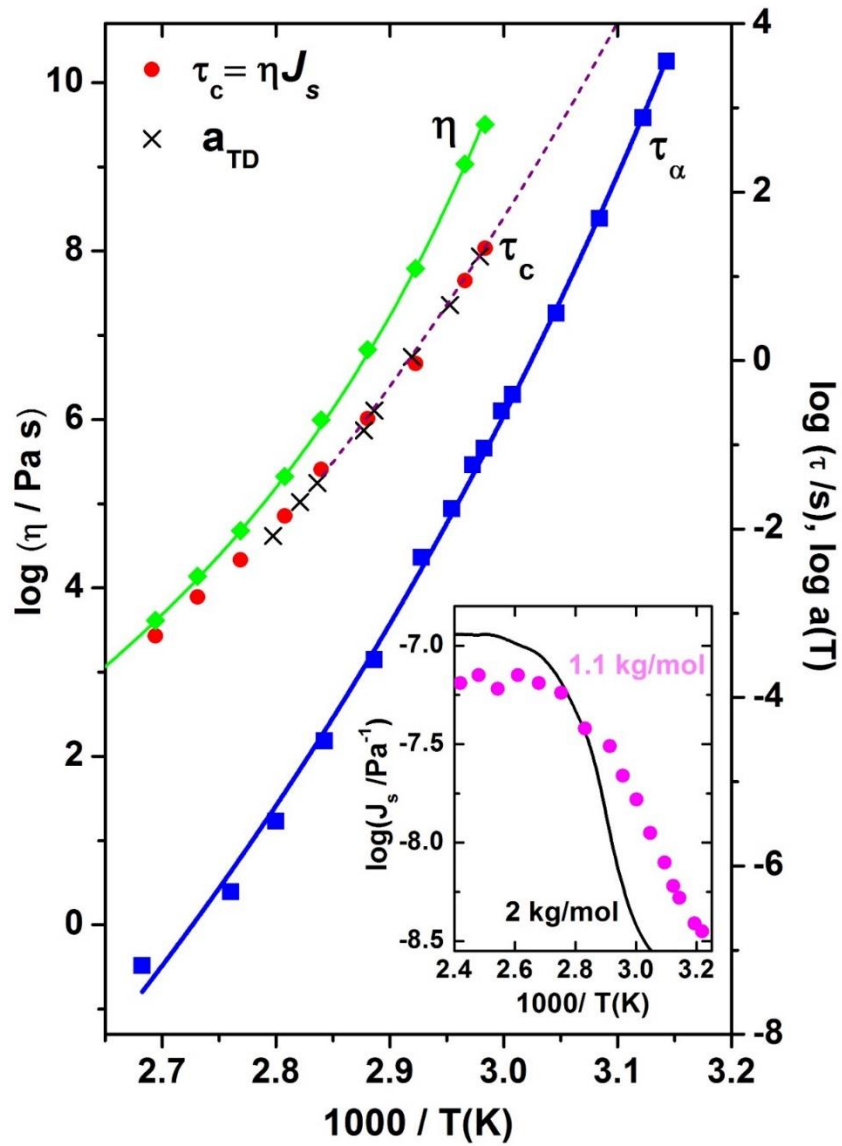


Figure 1. Arrhenius plot of various quantities of PS2k. Local segmental relaxation times<sup>15</sup>  $\tau_\alpha$  (blue squares), zero-shear rate viscosities  $\eta$  (green diamonds)<sup>20</sup>, the shift factors ( $a_{TD}$ ) for the translational relaxation times  $\tau_D$  obtained from the  $D_{cV}$  in ref. 20 ( $\times$ ), and the chain relaxation times ( $\tau_c$ ) calculated by the product  $\eta J_s$  (red filled circles)<sup>15</sup>. Left Y-axis is for the logarithm of the viscosity data, right Y-axis is for logarithm of relaxation times and shift factors. The two scales span over similar amount of decades and have been chosen to superpose  $\eta$  with  $\tau_c$  at the highest temperatures (not shown). The two solid lines are the VFTH fits to  $\tau_\alpha$  and the shifted  $\log \eta$ . The dashed line on top of  $a_{TD}$  and  $\tau_c$  has  $T$ -dependence calculated from that of  $\tau_\alpha$  according to eq.(2). The inset shows the  $T$ -dependence of the steady-state recoverable compliance  $J_s$  of PS2k<sup>15</sup> and PS1.1k.<sup>10</sup>

The decrease of  $J_s$  on lowering temperature towards  $T_g$  is a general property of low MW PS, as shown for PS2K and PS with MW=1.1 kg/mol in the inset, and other polymers elsewhere<sup>10,11,16-19</sup>. From these data of shear creep compliance, the chain shear relaxation time  $\tau_c$  is calculated by the product,  $\eta J_s$ . Also included in Figure 1 are the shift factors  $a_{TD}$  for the translational relaxation time,  $\tau_D$ , obtained from the bulk self-diffusion coefficients of PS2K.<sup>20</sup> The shift factors  $a_{TD}$  were chosen so that they overlap with the  $\tau_c$  in Figure 1. The overlap makes evident that the two chain relaxation times  $\tau_c$  and  $\tau_D$  have identical temperature dependence, but it is significantly weaker than that of  $\tau_\alpha$ . Thus the dynamics of chain modes are distinctly different from the structural  $\alpha$ -relaxation, and any explanation of enhanced diffusion of low MW PS at the free surface must address the polymer chain diffusion mode,

the size of the enhancement of its mobility at the surface, and its mobility gradient. The polymer chain mobility gradient is important for consideration of the effect due to the penetration of PS chains into the interior as pointed out before by ZY<sup>9</sup>.

The weaker  $T$ -dependence of  $\tau_c$  and  $\tau_D$  than  $\tau_\alpha$  of low MW PS is part of the comprehensive breakdowns of thermorheological complexity discovered by Plazek in the glass-rubber transition zone<sup>10-12</sup> as well as its relation to the terminal zone if the polymer is entangled.<sup>21,22</sup> The thermorheological complexities cannot be explained by conventional viscoelasticity theory, which has the same friction coefficient  $\zeta_0(T)$  for the  $\alpha$ -relaxation and all the chain modes, and consequently the same temperature dependence of their shift factors to predict instead thermorheological simplicity. The Coupling Model (CM) is different<sup>14,15,17,19,23</sup>. Due to interaction, any cooperative relaxation and diffusion are slowed down to some degree determined by the size of its coupling parameter.<sup>24</sup> For the  $\alpha$ -relaxation the slowing down is given in the CM by the stretched exponential function,  $\varphi(t) = \exp[(t/\tau_\alpha)^{1-n_\alpha}]$ , where  $n_\alpha$  is the coupling parameter of the  $\alpha$ -relaxation. The CM merely predicts the cooperative  $\alpha$ -relaxation function has the stretched exponential time dependence, but not the values of  $n_\alpha$  and  $\tau_\alpha$  for any polymer or glass-former in general. Notwithstanding, the values of these parameters at any temperature were obtained by comparison with the stretched exponential function directly obtained by experiments such as photon correlation spectroscopy (PCS)<sup>18,25,26</sup>, or by fitting the time dependence of creep compliance  $J(t)$ .<sup>18</sup> The PCS experimental value of  $n_\alpha$  at temperatures above  $T_g$  are 0.65 and 0.50 for high<sup>25</sup> and low<sup>26</sup> MW PS respectively. Another PCS study of poly(methylphenylsiloxane)<sup>18</sup> gave the value of  $n_\alpha=0.56$ . The Rouse chain modes within the glass-rubber transition zone are entropic and non-cooperative<sup>22,27</sup>, and hence their coupling parameter,  $n_R$ , has value zero. From the key result

of the CM, it follows that  $\tau_\alpha(T) \propto a_{T,\alpha} \propto [\zeta_o(T)]^{1/(1-n_\alpha)}$  and  $\tau_R(T) \propto a_{T,R} \propto [\zeta_o(T)]^{1/(1-n_R)}$ ,<sup>14,18,19,23</sup> where  $a_{T,\alpha}$  and  $a_{T,R}$  are respectively the shift factors. With the values of  $n_\alpha=0.64$  larger than  $n_R=0$ , which are independently obtained and not empirical adjustable parameters, these relations readily explain the weaker  $T$ -dependence of  $a_{T,R}$  than  $a_{T,\alpha}$  and thermorheological complexity of the glass-rubber transition zone<sup>10,11,13,21,22</sup>.

The shear compliance of the glass-rubber transition zone in high MW PS rises from the glassy compliance  $J_g=0.93 \times 10^{-9} \text{Pa}^{-1}$  up to the entanglement plateau compliance  $J_s \equiv J_{\text{plateau}} \approx 10^{-6} \text{Pa}^{-1}$ . Williams<sup>27</sup> had shown that the Rouse modes can only account for compliance  $J(t)$  larger than  $1.3 \times 10^{-7} \text{Pa}^{-1}$ , while the  $\alpha$ -relaxation contributes to the compliances in the range from  $J_g=0.93 \times 10^{-9} \text{Pa}^{-1}$  and up to  $J_{e\alpha} \approx 4 \times 10^{-9} \text{Pa}^{-1}$ .<sup>27</sup> The missing compliance from  $J_{e\alpha} \approx 4 \times 10^{-9} \text{Pa}^{-1}$  to  $J_{R0}=1.3 \times 10^{-7} \text{Pa}^{-1}$  has to be filled by contributions from another viscoelastic mechanism. It was found by experiments in high MW polyisobutylene<sup>13,14</sup>, PS<sup>29,30</sup> and other polymers<sup>30</sup>, and it has been referred to as the sub-Rouse modes. Thus the contribution  $J_{sR}(t)$  of the sub-Rouse modes to  $J(t)$  in the glass-rubber transition zone of PS falls within the range,

$$4 \times 10^{-9} \text{Pa}^{-1} \leq J_{sR}(t) \leq 10^{-7} \text{Pa}^{-1}, \quad (1)$$

The inset of Fig.1 shows the plateau compliance  $J_s(T)$  of PS2K<sup>15</sup> and PS with MW=1.1 kg/mol<sup>10</sup> measured at temperature above and down to the respective  $T_g$  of the two samples. It can be seen from the inset that  $J_s(T)$  lies within the range of  $J_{sR}(t)$  stipulated in eq.1. Therefore, for the PS samples studied by ZY<sup>9</sup> with molecular weights ranging from 1.1 to 3.0 kg/mol, the PS chain modes responsible for surface grating decay by diffusion are the sub-Rouse modes. The good agreement in  $T$ -dependence of  $\tau_c \equiv \tau_{sR}$  and  $a_{TD}$  shown in Fig.1 is equivalent to the shift factor  $a_{T,c} \equiv a_{T,sR}$  of  $\tau_c \equiv \tau_{sR}$  have the same  $T$ -dependence as  $a_{TD}$ , and hence

the coupling parameter  $n_{sR}$  of the sub-Rouse modes is the same as that of self-diffusion,  $n_D$ . The temperature dependence of  $a_{T,sR}$  and  $a_{TD}$  is given via the CM by  $a_{TD} = a_{T,sR} \propto [\zeta_o(T)]^{1/(1-n_{sR})} = [\zeta_o(T)]^{1/(1-n_D)}$ .<sup>14,18,19-22</sup> Comparing this expression for  $a_{TD}$  with that of  $a_{T,\alpha}$  given before, we have the relation,

$$\log a_{TD} = \left[ \frac{1-n_\alpha}{1-n_D} \right] \log a_{T,\alpha}. \quad (2)$$

Evaluating the right-hand-side of eq.2 with the ratio  $(1-n_\alpha)/(1-n_D)$  put equal to 0.81, the result represented by the dashed magenta line in Fig.1 captures well the  $T$ -dependence of  $\log a_{TD} = \log a_{T,sR}$ . Together with the value of  $n_\alpha$  of low MW PS estimated to be about 0.5<sup>26</sup> this result give an estimate of  $n_{D=n_{sR}}$ , which is approximately 0.38. Such a smaller value of  $n_{D=n_{sR}}$  for the PS chain diffusion mode compared with  $n_\alpha=0.50$  for the structural  $\alpha$ -relaxation of OTP<sup>3</sup> and 0.41 for IMC<sup>5</sup> means the enhancement of diffusion at the surface of PS is smaller than in the cases of IMC and OTP according to the CM (see eq.3 and the discussion immediately following it in ref.5). However the PS chains penetrate deeper into the interior as pointed out by others<sup>6-8</sup> and by ZY<sup>9</sup>. Larger the distance from the surface, smaller is the effect of the free surface in the reduction of  $n_D$ , and lesser is the corresponding enhancement of mobility of PS chains and the increase of chain diffusion constant. The effective surface diffusion constant  $\widehat{D}_{cS}$  of PS chains measured by surface grating decay is determined by the average of the reductions of  $n_D$  over the distance of penetration of the PS chains into the interior from the surface. After averaging, the enhancement of surface diffusion mobility of PS is further reduced from that obtained at the surface. The effects combined explain why the increase of surface diffusivity of PS measured by surface grating decay is much less than that of OTP and even less than IMC, although the coupling parameter  $n_\alpha$  of the structural  $\alpha$ -relaxation of bulk PS is about the same as OTP, and even larger than IMC.



In summary, we point out the obvious fact that surface diffusion of polystyrene (PS) is carried out by the polymer chain diffusion mode and not by the structural  $\alpha$ -relaxation. Based on the modification the structural  $\alpha$ -relaxation of small-molecule glass-formers at the free surface, extant theoretical explanations<sup>4,5</sup> of enhancement of surface diffusion are no longer applicable to account for the enhancement of surface diffusion of PS observed by ZY<sup>6</sup> in surface grating decay experiment. Solution of the new problem requires understanding of the change of polymer chain diffusion mode due to the presence of the free surface, which is different from the corresponding change of the structural  $\alpha$ -relaxation because of thermorheological complexity of polystyrene. In addition, the PS chain mobility gradient away from the surface together with the deeper penetration of polymer chains into the interior has to be considered, in accord with the suggestion of ZY<sup>9</sup>. Applied to surface polymer chain diffusion, the results from the CM are consistent with the much reduced enhancement of surface diffusion in PS glass<sup>9</sup> compared with *o*-tphenyl<sup>3</sup> and indomethacin<sup>1</sup> observed by the surface grating decay method. Further advance may come from the ECNLE theory for the  $\alpha$ -relaxation of free-standing films<sup>6,7</sup> by extending it to consider the sub-Rouse modes of free-standing films.

#### AUTHOR INFORMATION

Corresponding Author

\*E-mail [kia.ngai@pi.ipcf.cnr.it](mailto:kia.ngai@pi.ipcf.cnr.it)

[ngaikia@gmail.com](mailto:ngaikia@gmail.com)

#### REFERENCES

- (1) Zhu, L.; Brian, C. W.; Swallen, S. F.; Straus, P. T.; Ediger, M. D.; Yu, L. Surface Self-Diffusion of an Organic Glass. *Phys. Rev. Lett.* **2011**, *106*, 256103.

- (2) Brian, C. W.; Yu, L. Surface Self-Diffusion of Organic Glasses. *J. Phys. Chem. A* **2013**, *117*, 13303–13309.
- (3) Zhang, W.; Brian, C. W.; Yu, L. Fast Surface Diffusion of Amorphous o-Terphenyl and its Competition with Viscous Flow in Surface Evolution. *J. Phys. Chem. B* **2015**, *119*, 5071–5078.
- (4) Stevenson, J. D.; Wolynes, P. G. On the Surface of Glasses. *J. Chem. Phys.* **2008**, *129*, 234514.
- (5) Capaccioli, S.; Ngai, K. L.; Paluch, M.; Prevosto, D. Mechanism of Fast Surface Self-Diffusion of an Organic Glass. *Phys. Rev. E* **2012**, *86*, 051503.
- (6) Mirigian, S.; Schweizer, K. S. Slow relaxation, spatial mobility gradients, and vitrification in confined films, *J. Chem. Phys.* **2014**, *141*, 161103.
- (7) Mirigian, S.; Schweizer, K. S. Theory of activated glassy relaxation, mobility gradients, surface diffusion, and vitrification in free standing thin films, *J. Chem. Phys.* **2015**, *143*, **143**, 244705.
- (8) K. L. Ngai, Interpreting the Dynamics of Nano-Confined Glass-Formers and Thin Polymer Films: Importance of Starting from a Viable Theory for the Bulk, *J. Polym. Sci.: Part B: Polym. Phys.* **2006**, *44*, 2980–2995.
- (9) Zhang, W.; Yu, L. Surface Diffusion of Polymer Glasses, *Macromolecules* **2016**, *49*, 731–735.
- (10) Plazek, D. J.; O'Rourke, M. Viscoelastic Behavior of Low Molecular Weight Polystyrene, *J. Polym. Sci. Polym. Phys. Ed.* **1971**, *9*, 209-243.
- (11) Ngai, K. L.; Plazek, D. J. Identification of different modes of molecular motion in polymer that cause thermorheological complexity, *Rubber Chem. Tech. Rubber Review* **1995**, *68*, 376.
- (12) Plazek, D. J. 1995 Bingham Medal Address: Oh, thermorheological simplicity, wherefore art thou? *J. Rheology* **1996**, *40*, 987.
- (13) Plazek, D. J.; Chay, I. C.; Ngai, K. L.; Roland, C. M. Viscoelastic properties of polymers 4.: thermorheological complexity of the softening dispersion in polyisobutylene, *Macromolecules* **1995**, *28*, 6432-6436.
- (14) Ngai, K. L.; Plazek, D. J.; Rizos, A. K., Viscoelastic Properties of Amorphous Polymers. 5. A Coupling Model Analysis of the Thermorheological Complexity of

- Polysisobutylene in the Glass–Rubber Softening Dispersion, *J. Polymer Sci. B: Polym.Phys.* **1997**, *35*, 599-614.
- (15) Roland. C.M.; Ngai, K.L.; Plazek, D.J. Modes of molecular motion in low molecular weight polystyrene, *Macromolecules* **2004**, *37*, 7051-7055.
- (16) Gray, R.W.; Harrison G. ; Lamb, J. Creep compliance of low molecular weight polystyrene, *Proc.R.Soc.Lond.* **1977**, *A 356*, 77.
- (17) Ngai, K.L.; Plazek, D.J.; Deo, S.S., Physical Origin of the Anomalous Temperature Dependence of the Steady-State Compliance of Low Molecular Weight Polystyrene, *Macromolecules* **1987**, *20*, 3047.
- (18) Plazek, D.J.; Bero, C.; Neumeister, S.; Floudas, G.; Fytas, G.; K.L. Ngai, Viscoelastic properties of amorphous polymers 3: low molecular weight poly(methylphenylsiloxane), *Colloid Polym. Sci.* **1994**, *272*, 1430.
- (19) Plazek, D.J.; Schönhals, A.; Schlosser, E.; Ngai, K.L. Breakdown of the Rouse model for polymers near the glass transition Temperature, *J. Chem. Phys.* **1993**, *98*, 6488.
- (20) Urakawa, O.; Swallen, S. F.; Ediger, M. D.; von Meerwall, E. D. Self-Diffusion and Viscosity of Low Molecular Weight Polystyrene Over a Wide Temperature Range, *Macromolecules* **2004**, *37*, 1558–1564.
- (21) Plazek, D.J. The Temperature Dependence of the Viscoelastic Softening and Terminal Dispersions of Linear Amorphous Polymers, *J.Polym.Sci. Polym.Phys. ed.* **1982**, *20*, 729-742.
- (22) Ferry, J.D. *Viscoelastic Properties of Polymers*, 3<sup>rd</sup> ed. 1980, Wiley, NY.
- (23) Ngai, K.L.; Plazek, D.J.; Rendell, R.W. Some examples of possible descriptions of dynamic properties of polymers by means of the coupling model, *Rheol. Acta* **1997**, *36*, 307-319.
- (24) Ngai, K.L. *Relaxation and Diffusion in Complex Systems*, Springer, NY **2010**.
- (25) Patterson, G. D. *Dynamic Light Scattering*, Chapter 6, p. 260, R. Pecora, Ed., Academic, New York, (1986).
- (26) Rizos, A.K.; Ngai, K.L. Local Segmental Dynamics of Low Molecular Weight Polystyrene: New Results and Interpretation *Macromolecules* **1998**, *31*, 6217-6225.
- (27) Williams, M.L. Upper limit of the shear modulus calculated from the Rouse theory, *J. Polym. Sci.* **1962**, *62*, S7–S8.

- (28) Ngai, K.L.; Plazek, D.J.; Echeverria I. Viscoelastic Properties of Amorphous Polymers. 6. Local Segmental Contribution to the Recoverable Compliance of Polymers, *Macromolecules* **1996**, *29*, 7937-7942.
- (29) Ngai, K.L.; Plazek, D.J. Resolution of Sub-Rouse Modes of Polystyrene by Dissolution, *Macromolecules* **2002**, *35*, 9136-9141.
- (30) Paluch, M; Pawlus, S.; Sokolov, A.P.; Ngai, K.L. Sub-Rouse Modes in Polymers Observed by Dielectric Spectroscopy, *Macromolecules* **2010**, *43*, 3103–3106]

Table of Contents Graphics –

“ Surface Diffusion of Polymer Glasses Redux” , K. L. Ngai and Simone Capaccioli

