1. INTRODUCTION

It is well known that block copolymers possess order-disorder transition (ODT) at a certain condition determined by Flory-Huggins interaction parameter $\chi$, degree of polymerization $N$, and composition $\phi$, which can be basically explained by Leibler’s theory.\(^1\) Composition dependence of equilibrium nanophase-separated structures for well characterized AB, BAB and ABC block copolymers and also for AB2 star-branched copolymers are summarized by Matsushita.\(^2\)

In the so-called weak segregation regime near the ODT, thermal fluctuations of composition existing in a length scale of the copolymer chain and the viscoelastic heterogeneity of components influence phase behavior and viscoelastic properties of block copolymers.\(^3\) In the strong segregation regime, nanophase separated structure of block copolymers reaches equilibrium states in chain length scale. In the larger scale, however, the structure is randomly oriented multigrain structure which is dependent on thermal and flow history. These structural characters and the viscoelastic heterogeneity of components are the reasons for very complicated rheological properties of block copolymers. Relationships between structures and viscoelastic properties of block copolymers are also summarized in some review articles.\(^7\)\(^-\)\(^13\) A brief summary of results related with this paper is as following.

The most well studied relationships between structure and rheology of block copolymers are those for lamellar forming diblocks. In the quiescent disordered states, it was reported that the fluctuation effects are more pronounced on the viscoelastic properties than those on scattering data.\(^14\) Both
storage, $G'(\omega)$, and loss, $G''(\omega)$, moduli are enhanced due to the fluctuation effects at lower frequency $\omega$, that is in terminal region. The enhancement of modulus by the fluctuation effects was more obvious for $G'$ than for $G''$. In a few studies, flow induced ordering are reported in the quiescent disordered states close to the ODT. \(^{13,19}\)

In the quiescent ordered states, $G'(\omega)$ and $G''(\omega)$ show power law dependence on $\omega$ ($G', G'' \sim \omega^{1/2}$) at the low $\omega$ end. \(^{14,15,20}\) This behavior can be theoretically explained by the large scale motions of randomly oriented grains/defects \(^{21}\) and/or by chain relaxation mechanism of entangled component polymers (chain retraction modes). \(^{22}\) It was observed that $G'$ and $G''$ values in the power law region become smaller when lamellae are preferentially aligned parallel and perpendicular to the flow direction in which lamellar normals are parallel to shear gradient and vorticity directions, respectively. \(^{23-25}\) The effect of alignment was more pronounced in the latter case. When the structure is well aligned, $\omega$ dependencies of $G'$ and $G''$ become similar to those of uniform polymeric liquids.

In a previous paper, \(^{26}\) we reported that shear rate, $\dot{\gamma}$, dependence of first normal stress difference $N_1$ changes from textured fluid like behavior ($\sim \dot{\gamma}$) to uniform polymeric liquid like behavior ($\sim \dot{\gamma}^{1/2}$) when the lamellae are well aligned for polystyrene-block-polyisoprene (SI) in DOP solutions near ODT. When polymeric liquid like behaviors are observed at the well aligned state like above cases, the power law behavior of $G'$ and $G''$ can be attributed to the responses from grain/defect motions. \(^{27}\) Apparent zero shear viscosity $\eta_0$ and steady state compliance $J_c$ can be obtained from polymeric liquid like behaviors but they cannot be precisely compared with those of components due to the differences of components’ viscoelastic properties.

To compare viscoelastic properties of diblock copolymers and component homopolymers, the behaviors of symmetric poly(styrene-block-2-vinylpyridine) $\chi$ (SP)s, having almost the same components’ viscoelastic properties \(^{28}\) as well as other physical properties \(^{33-35}\), are studied under the dynamic and steady shear flow in a common good solvent near the ODT. \(^{29,31}\) Corresponding structural changes under the flow are examined by small angle neutron scattering (SANS) using deuterated SP (DP). \(^{30,31,36-38}\)

In the disordered states \(^{39}\), no fluctuation effect was observed on $G''$ and shear stress $\sigma$ so that the $\eta_0$ values obtained by dynamic and steady flow measurements are practically the same as those for components’ solutions. \(^{32,39}\) In contrast, $J_c$ obtained by dynamic measurements are higher than those for components. Under steady shear flows, however, SANS intensities became lower than quiescent state and $J_c$ became almost the same as those of components denoting the suppression of fluctuation effects. Even in the quiescent ordered states \(^{30,31}\), $\eta_0$ data can be obtained under steady flow, which are consistent with those for components. On the other hand, $\dot{\gamma}$ dependence of $N_1$ changed similarly as SI solutions. When $N_1$ became proportional to $\dot{\gamma}^{1/2}$ at higher $\dot{\gamma}$, flow-SANS intensities showed strong anisotropy denoting perpendicular alignment of lamellar structure. The values of $J_c$ obtained in well aligned states are practically the same as those of components.

We further compared flow-induced alignments of DI (deuterated SI) and DP solutions by flow-SANS having similar values of effective $\chi N$ determined by ordinary SANS measurements without any correction. \(^{40}\) It was reported that the degree of perpendicular alignment is primarily determined by effective $\chi N$ and reduced shear rates, $\dot{\gamma}/\dot{\gamma}^*$, irrespective of the components’ viscosity ratio, where $\dot{\gamma}^*$ is the critical $\dot{\gamma}$ for non-Newtonian behavior. The parallel alignment becomes minor near the ODT and/or at high $\dot{\gamma}$ and such tendency is pronounced for the samples whose viscosity ratio of components is close to 1, that is for SP, qualitatively consistent with the theory of Fredrickson. \(^{41}\)

In the above studies, it was shown that molecular weight and concentration dependencies of $\eta_0$ and $J_c$ for SPs in disordered and well aligned ordered states are the same as those of component polymer solutions over wide ranges of molecular weight and concentration. However, all the data are in a very narrow range of effective $\chi N$ close to ODT. In addition, it was observed that fluctuation effects in SP solutions are very weak compared to SI solutions.

To further examine the viscoelastic properties of block copolymers, it is very interesting and essential to study SP diblocks in comparison with components for more wider range of $\chi N$ in melt states, where stronger fluctuation effects are expected as shown by a previous study. \(^{29}\) In this study, we examine viscoelastic properties of ordered and disordered symmetric SP diblocks having relatively low molecular weights at melt under steady shear flow based on the temperature dependence of $\chi$ obtained for the same DP sample in the previous study \(^{29}\) in a wider range of temperature.

2. EXPERIMENTAL SECTION

2.1 Samples

The SP diblock copolymers and polystyrenes (PS) are synthesized by anionic polymerization in vacuo as reported previously. \(^{34,35}\) Weight-averaged molecular weights $M_w$ of the samples are determined by multi-angle laser light scattering (MALLS) method using DOWN EOS enhanced optical
system of the Wyatt Technology at 35 °C in THF after optical purification with 0.2 µm PTFE filter. The wave length used was 690 nm and the reflective index increment, \(dn/dc\), used was 0.185 mL/g for PS in THF, since the value for poly-(2-vinylpyridine) (P2VP), 0.180 mL/g is very close to the former.

Molecular weight heterogeneities, \(M_n/M_w\) ( \(M_n\) : number-averaged molecular weights) are determined in THF by a GPC system of Tosoh Ltd., equipped with RI-8012 differential refractive index detector using three GMHHR columns and PSSs as standards. Volume fractions of styrene in SP \(\phi_s\) are determined by \(^1\)H NMR spectra measured with a Varian unity-500 NMR spectrometer.

Glass transition temperature, \(T_g\) of SP samples are determined by DSC measurement using Seiko Instruments Inc., DSC6220 at heating rate of 5 °C/minutes. Molecular characteristics of SPs and PSs are tabulated in Table I. ODTr temperature, \(T_{ODT}\) of SP29 was determined as 135 – 138 °C by dynamic mechanical analysis (DMA) in a previous work.\(^{29}\) Since \(T_{ODT}\) for other \(M_n\) samples cannot be determined by DMA, we determined temperature, \(T\), dependence of \(\chi\) parameter by SANS measurement using the same deuterated sample DP17 (\(M_n: 1.2\times10^4\), \(M_w: 1.05\)) in a much wider \(T\) range than in the previous work.\(^{29}\) Using the \(T\) dependence of \(\chi\), ODTr of other samples are estimated. Then the states of a few samples are confirmed by small angle X-ray scattering (SAXS) measurements at selected \(T\)s.

### 2.2 SANS measurement

DP17 was sealed into a 2 mm thick conventional quartz cell for liquid after evacuating it at melt state to prevent from producing bubbles during SANS measurements. The SANS measurement was performed on SANS-U spectrometer\(^{43}\) of the Institute for Solid State Physics, the University of Tokyo, installed at the JRR-3 research reactor of JAEA, Tokai, Japan. The wavelength, \(\lambda\), of neutrons used was 0.70 nm and the sample-to-detector distance was 3.0 m. Each measurement was conducted for 30 or 40 minutes in data acquisition period at different temperature, \(T\), ranging from 80 to 184 °C.

All the scattering patterns observed on a two-dimensional position-sensitive detector were isotropic, so that they were circularly averaged into the scattering intensity, \(I(q)\), profiles as a function of the wave vector, \(q\), defined as \((4\pi/\lambda) \sin\theta\), where \(2\theta\) is the scattering angle. All \(I(q)\) profiles were corrected for incoherent scattering using hydrogenous P2VP, and converted into the absolute intensity in the unit of \(\text{cm}^{-1}\) using standard Lupolen.

#### 2.3 SAXS measurements

Small angle X-ray scattering (SAXS) measurements are performed by SAXSess mc\(^2\) equipped with TCS120 thermo-controll chamber at the show room of Anton Paar Japan. The X-ray beam generated by 3.5 kW generator is collimated by Kratky block collimator (Kα line, \(\lambda = 0.154 \text{ nm}\)) and scattered beam is detected by an imaging plate.\(^{43}\) Powder like samples of SP29, SP107, and SP105 are put into powder cell and measured at 117 °C for SP29 and SP107, and at 100 °C for SP105. The data acquisition time was 12 minutes for each sample. All the scattering patterns observed were isotropic so that circularly averaged \(I(q)\) profiles are obtained after desmearing of the data and background (empty cell) subtraction.\(^{43}\)

#### 2.4 Rheological Measurements

Disk shaped samples for rheological measurements are prepared by moulding at around 150 °C and annealed in vacuum oven to get rid of bubbles before the measurements. Steady shear flow measurements are carried out with a TA Instruments ARES rheometer using 8 mmφ and 0.1 rad cone angle cone plates at 160 °C. First, transient behaviors are examined for each sample at a few selected shear rates. Steady state values of stresses are reached almost instantaneously for the samples in the disordered state, while it took about 3 to 7 minutes to reach steady values for those in the ordered states and the steady values showed relatively large irregular vibrations. Therefore, 10 minutes duration of the flow was employed before 5 minutes data acquisition to obtain steady state data in the ordered states.

DMA in linear region (maximum strain: 1 %) are performed with an Anton Parr MCR300 rheometer using 8 mmφ parallel plates in a temperature range of 170-120 °C for 4 lower \(M_n\) samples. All the measurements are carried out under \(N_2\) gas after at least 10 minutes duration time before the measurement at each temperature.

### Table I. Characteristics of poly(styrene-b-2-vinyl-pyridine)s.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>(M_n^*)</th>
<th>(M_w/M_n)</th>
<th>(\phi_s)</th>
<th>(T_{ODT}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP106</td>
<td>0.47×10^4</td>
<td>1.02</td>
<td>0.51</td>
<td>87.0</td>
</tr>
<tr>
<td>SP105</td>
<td>0.81×10^4</td>
<td>1.02</td>
<td>0.52</td>
<td>88.0</td>
</tr>
<tr>
<td>SP107</td>
<td>1.25×10^4</td>
<td>1.02</td>
<td>0.51</td>
<td>89.8</td>
</tr>
<tr>
<td>SP29</td>
<td>1.52×10^4</td>
<td>1.03</td>
<td>0.52</td>
<td>90.2</td>
</tr>
<tr>
<td>SP27</td>
<td>2.1×10^4</td>
<td>1.03</td>
<td>0.50</td>
<td>-</td>
</tr>
<tr>
<td>SP102</td>
<td>2.90×10^4</td>
<td>1.01</td>
<td>0.52</td>
<td>-</td>
</tr>
<tr>
<td>SP101</td>
<td>4.69×10^4</td>
<td>1.04</td>
<td>0.51</td>
<td>-</td>
</tr>
<tr>
<td>PS-9.6k</td>
<td>0.96×10^4</td>
<td>1.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PS-19.6k</td>
<td>1.96×10^4</td>
<td>1.02</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^*\) by MALLS. \(^*\) by GPC. \(^\dagger\) by \(^1\)H-NMR. \(^\ddagger\) by DSC.
3. RESULTS AND DISCUSSIONS

3.1 ODT and $\chi$ parameter for SPs

Figure 1 shows plots of $I(q)$ vs. $q$ for DP17 at different $T$. All the profiles exhibit only one broad peak without any higher-order peaks from ordered structure. The peak intensity, $I_m$, first increased when $T$ was increased up to 92 °C, which is close to $T_g$ (91 °C), determined previously and then decreased with further increasing $T$. The shape of $I(q)$ becomes broader, and the peak position, $q_m$, is slightly shifted to higher $q$ with increase of $T$ above $T_g$. The latter indicates that characteristic length, $D$, defined as $2\pi/q_m$ corresponding to chain dimension, decreases gradually with increase of $T$.

Sakamoto and Hashimoto intensively examined ODT of SI with low molecular weight by using SAXS. They characterized the phase behavior of SI at high temperature ($T > T_g$) by defining two characteristic temperatures: $T_{ODT}$ and the critical temperature, $T_{MF}$, for the mean-field theory. At $T < T_{MF}$ thermal fluctuation effect cannot be ignored. To estimate the $\chi$ values as exactly as possible without the thermal fluctuation effect, $T_{MF}$ was first determined for DP17, following the methods employed by Sakamoto and Hashimoto.

Figure 2 shows plots of $I_m^{-1}$ and the square of the half-width at half maximum, $\sigma_q^2$, of the observed peak as a function of $T^{-1}$ for DP17. In this figure, $T_g$ and median value of $T_{ODT}$, 93-102 °C for DP17, consistently determined with highly concentrated solutions of DP17, are indicated by the vertical broken lines. Both $I_m^{-1}$ and $\sigma_q^2$ exhibited linear relationship against $T^{-1}$ as shown by respective straight lines at sufficiently low $T^{-1}$, that is, at sufficiently high $T$, according to the prediction of the mean-field theory. The deviations of $I_m^{-1}$ and $\sigma_q^2$ from the straight lines due to the thermal fluctuation effect occur at almost the same $T$, corresponding to $T_{MF}$ (around 152 °C). The extrapolated straight lines coincided on the abscissa at a $T^{-1}$, which corresponds to the mean-field spinodal temperature. From these results, we can say that fluctuation effects are apparently observed in wide range of experimental window for low molecular weight samples in melt state, unlike to the case of SP solutions.

The value of $\chi$ was evaluated at each $T$ by analyzing SANS profiles with the mean-field theory of Leibler corrected for the polydispersity, $M_p/M_n$, of 1.05 in molecular weight. However, the asymmetry in segmental volume between PS and P2VP was not taken into account, since they possess the same statistical segment length. The evaluated values of $\chi$ and $D$ are represented against $T^{-1}$ in Figure 3. In this figure, $T_{MF}$, $T_{ODT}$, and $T_g$ determined above are indicated as the vertical broken lines together. Both $\chi$ and $D$ gradually increase with increasing $T^{-1}$, that is, decreasing $T$. The increment in $D$ slightly changes at around $T_{MF}$, but it is not clearly observed as reported for PS-PI. The value of $D$ increases with increase of $T^{-1}$, up to the value in the ordered state (lamellar spacing). The lamellar spacing at around room temperature is consistent...
with those for symmetric SPs in the previous work.\textsuperscript{2)}

T-dependence of $\chi$ was evaluated from the linear relationship observed below $T_M$\textsuperscript{1}, that is, above $T_M$ for DP17 as

$$\chi = 0.0072 + 30/T (K).$$

Since molecular weights of SP105 and SP106 are lower than that of DP17, we can safely assume that $T_{ODT}$ of these samples are below their $T_g$. Estimated mean field $\chi$ values for SP105 and SP106 at 160 °C are 5.7 and 3.3, respectively. For higher molecular weight samples, SP27, SP102, and SP101, it is expected that these samples are in the ordered states even at the highest experimentally accessible temperatures, say at 240°C. For SP27, however, we may say that this sample is in weak segregation regime (mean field $\chi$ value: 14 at 160°C). If we allow 10% experimental error, $T_{ODT}$ for SP29 determined by DMA become consistent with the estimated value using above $T$ dependence of $\chi$. For SP107, it is expected that $T_{ODT}$ is somewhere around 105 - 120 °C. This estimation was further examined by SAXS measurements.

3.2 Viscoelastic Properties

Figure 5 shows double logarithmic plots of $\sigma$ and $N_1$ at steady states against $\dot{\gamma}$ for SP27, SP102 and SP101 at 160 °C. The values obtained by transient measurements for SP27 are also shown in Fig. 5(a) by filled symbols. Note that the steady values cannot be approached at lower $\dot{\gamma}$ since stresses continuously decreased very gradually, while the sample became instable at higher $\dot{\gamma}$ so that the data are limited in narrow range of $\dot{\gamma}$ regimes. The data for SP27 (Fig. 5(a)) shows transition from textured fluid like behavior to uniform polymeric liquid like behavior with increase of $\dot{\gamma}$, though the data are scarce at low $\dot{\gamma}$. From $\sigma$ and $N_1$ data at higher $\dot{\gamma}$ regime, where polymeric liquid like behavior is observed, apparent $\eta$ and $J_e$ for SP27 in the well aligned ordered states can be obtained. For SP102 and SP101, only textured fluid like behavior is observed as shown in Figure 5 (b) and (c). We also tried to measure steady state values for higher molecular weight sample but steady state was not attained at all, say within 30 minutes.

We could not succeed the steady flow measurement for the lowest molecular weight sample, SP106 due to its very low $\eta$. Figure 6 shows double logarithmic plots of $\eta$ and $J_e$ against $\dot{\gamma}$ for 3 other samples in the disordered states at 160 °C. The $\dot{\gamma}$ dependences of $\eta$ and $J_e$ for the second lowest

![Fig. 4. Plots of $I$ vs $q$ obtained by SAXS measurements. Symbols are denoted in the figure.](image)

![Fig. 5. Double logarithmic plots of $\sigma$ and $N_1$ at steady states against $\dot{\gamma}$ for (a) SP27, (b) SP102 and (c) SP101 in the ordered state at 160 °C. Symbols are denoted in the figure. Slopes of solid and dashed lines are 1 and 2, respectively.](image)
molecular weight sample, SP105 shown in Figure 6(a) are similar to those of typical uniform polymeric liquids so that \( \eta \) and \( J_e \) can be obtained by usual manner. With increase of molecular weight, or in other words approaching to ODT, striking features are observed for \( \dot{\gamma} \) dependence of \( \eta \). That is, two constant values for \( \eta \) can be obtained for SP107 and SP29. Hereafter, the constant \( \eta \) values at lower and higher \( \dot{\gamma} \) are designated as \( \eta^1 \) and \( \eta^2 \) for simplicity. As clarified from SANS measurements for DP17, fluctuation effects apparently exist in melt state near the ODT so that we can attribute higher \( \eta^0 \) to fluctuation effects.

According to the previous studies, \(^{30,31,40}\) there are 2 possible understanding for the data at high \( \dot{\gamma} \), that is, flow induced ordering and alignment or flow suppression of fluctuations. However, as pointed out in the previous work \(^{40}\), flow induced ordering did not occur for SP solution having similar effective \( \chi N \) at which DP solution showed flow induced ordering. When viscoelastic contrast of block components is large, tentative domains induced by composition fluctuations results in hard and soft domains which tend to phase separate under the flow. On the other hand, when viscoelastic contrast of block components is small, which is the case for SP, it can flow homogeneously so that composition fluctuation can be easily dissipated by the flow.

Together with the fact that the transient behaviors of these samples are different from those in the ordered states as mentioned in experimental section, and the fact that immediately repeated measurements are consistent with first ones, we speculate that there exists no ordered structure after the flow for these samples. Therefore, we tentatively conclude that the higher \( \eta^1 \) and the lower \( \eta^2 \) values are due to the fluctuation effects and their suppression by the flow with higher \( \dot{\gamma} \), respectively. To get definite conclusion, it is essential to confirm the structure of corresponding deuterated sample at similar experimental conditions by flow SANS, which is unfortunately not available now. Even if flow induced ordering taking place at high \( \dot{\gamma} \), the following discussions are not seriously affected. The constant values of \( J_e \) for SP107 and SP29 can be obtained at \( \dot{\gamma} \) range where \( \eta^0 \) are obtained. These data are discussed with data obtained by DMA mentioned below.

Figure 7 compares master curves of dynamic moduli \( (G'(\omega) \) and \( G''(\omega)) \) for SP29 and SP105 with those of PS having similar \( N \) at 160 °C. It is clear that the data in the transition region for SP and PS are practically the same, while the data for SP are higher than those of PS in the terminal region which are more pronounced for \( G' \) than for \( G'' \). Note that \( M_e \) of SP29 is lower than that of PS-19.6k so that the higher values of \( G' \) and \( G'' \) cannot be attributed to residual difference of \( N \). It is natural to conclude that enhancement of \( G' \) and \( G'' \) in terminal region is due to the fluctuation effects, which will be discussed later with the behaviours of other data.

![Fig. 6. Double logarithmic plots of \( \eta \) and \( J_e \) against \( \dot{\gamma} \) for (a) SP105, (b) SP107 and (c) SP29 in the disordered states at 160 °C. Symbols are denoted in the figure.](image1)

![Fig. 7. Double logarithmic plots of \( G' \) and \( G'' \) against \( \omega \) for SP29 and SP105 in the disordered state at 160 °C. Data for PS having similar \( N \) are also shown for comparison. Symbols are denoted in the figure.](image2)
Figure 8 summarizes master curves of SP samples in the disordered states. Temperature dependences of shift factors $\alpha_T$ (not shown, see Fig. 2 in ref. 46) used to generate these master curves are almost the same as those for components, P2VP$^{32}$ and PS.$^{45}$ However, there are slight differences from the data for high molecular weight samples reflecting their lower $T_g$. Therefore, the data in Figure 8 are further shifted to iso-free volume states referring the data for PS-19.6k, though the shifts are small. From these data, $\eta^0$ and $J_e$ are obtained by ordinary methods and compared with those obtained under steady shear flow.

Figure 9 shows double logarithmic plots of $\eta^0$ and $J_e$ vs. $M_w$ obtained from the data in Figs. 5(a), 6, and 8. The data for PS, which are consistent with previous studies for PS and P2VP$^{32,45}$, are shown by thick solid lines. The dashed lines are guide for eyes. It is clear in Fig. 9 (a) that the $\eta^0$ for SP105 ($M_w$: 8.1k) obtained by DMA and steady flow coincide with each other. In addition, the $\eta^0$ for two low $M_w$ samples by DMA are close to the data for PS. Since $T_{MF}$ was 152 °C for DP17 (mean field $\chi N$: about 8), it may be reasonable to say that fluctuation effects become very weak for $\sigma$ and $G''$ for SP106 and SP105 having lower mean field $\chi N$ at 160 °C. In Figure 9(b), it is seen that $J_e$ value for SP106 is close to that of PS. However, the $J_e$ values obtained for 3 samples in the disordered state are all higher than those of PS, implying that fluctuation effects are more pronounced for elastic behaviors than for $\eta$, qualitatively consistent with previous studies.$^{15-19}$

In the fluctuation regime near the ODT, chain conformation of block copolymer fluctuates between elongated one due to the repulsion of component chains of block copolymer and unperturbed one. Since the repulsion force become stronger by approaching ODT so that average chain length ($D$ in Figure 3) increase, which results in the higher values of elastic parameters than unperturbed polymer chain. Also the block copolymers tend to segregate so that tentative microdomains are formed, which are dissipated by the thermal motions of chains. The tentative structure sustains the stress and interface therein retards the dissipative motion of chains. The size of the tentative structure become larger and its life time become

![Figure 8](image1.png)

**Fig. 8.** Comparison of master curves for SP29, SP107, SP106 and SP105 in the disordered state at 160 °C. Solid lines denote the data for PS-19.6. Other symbols are denoted in the figure.

![Figure 9](image2.png)

**Fig. 9.** Double logarithmic plots of (a) $\eta^0$ and (b) $J_e$ vs. $M_w$ obtained from DMS and steady flow measurements in the disordered state. The data for ordered state (SP27) obtained at well aligned state and by subtraction method$^{46}$ are also shown for comparison. Symbols are denoted in the figure. Solid line denotes data for hPS. Dashed lines are guide for eyes.
longer by approaching ODT. These characteristics are the reasons for broader distribution of relaxations for diblocks compared to corresponding hPS (Figure 7), the enhancement of $\eta^0$ and $J_e$ and their higher $M_w$ dependencies compared to hPS.

Since all the theoretical studies concerned with enhancement of viscoelastic parameters due to the fluctuation effects assumes entangled systems, whereas all the data in this studies are those for non-entangled samples, we avoid direct comparison of the experimental results (such as slopes of dashed line) with theories and limit the discussion to the $\chi N$ range of fluctuation effects and their suppression by the flow.

It is also clear in Fig. 9 (a) that $\eta^0$ obtained by DMA and $\eta^0_1$ fall on the dashed line, while $\eta^0_2$ are close to the solid line for SP107 and SP29. These results imply that $\eta^0$ and $\eta^0_1$ obtained by DMA are values with enhancement due to fluctuation effects, while the lower values of $\eta^0_2$ than $\eta^0$ and $\eta^0_1$ are due to the suppression of fluctuation effects by shear flow with high $\dot{\gamma}$. In addition, the $J_e$ values from steady shear in Figure 9(b) are slightly higher than those from DMA. This feature may mean that $N_f$ is not so much suppressed as viscosity. However, concerning the difficulties of measurements with small geometries and larger error in $G'$ and $N_f$, the difference between data from steady shear and DMA may be within the experimental error so that we cannot get definite conclusion about the flow suppression of fluctuation effects for $N_f$. From the overall features of Figure 9, we can at least conclude that fluctuation effects on viscoelastic properties completely disappear at around $\chi N < 2 - 3$ for SPs.

The data for SP27 ($M_w : 21k$) in the ordered state are also shown in Figure 9. The data obtained by separation method of grain/defect and chain responses in $G'$ and $G''$ discussed in a separate paper (open symbols) are consistent with the data in disordered state. The data obtained at well aligned state are also consistent with other data in the disordered state. Therefore, we can conclude that no discontinuity of $\eta^0$ and $J_e$ occur by ODT for SP melts, consistent with the results for SP solutions.

### 3.3 Conclusions

Viscoelastic properties of symmetric poly(styrene-block-2-vinylpyridine)s, having almost the same components’ viscoelastic properties, in the ordered and disordered states under steady shear flow are examined for relatively low molecular weight samples at melt based on the temperature dependence of $\chi$. In the disordered state near the ODT, two constant values for $\eta$, $\eta^0_1$ and $\eta^0_2$ at lower and higher $\dot{\gamma}$, respectively are obtained and $\eta^0_1$ coincided with the value obtained by DMA. The constant values of $J_e$ are obtained at $\dot{\gamma}$ range where $\eta^0_2$ are obtained. It was concluded that higher $\eta^0_1$ and lower $\eta^0_2$ values are due to the fluctuation effects and their suppression by the flow with higher $\dot{\gamma}$, respectively. In the ordered state, well aligned state was only attained for the sample having lowest molecular weight. The values of $\eta^0$ and $J_e$ obtained in well aligned state are consistent with those in disordered state, denoting that there is no discontinuity of data due to ODT. It can be also concluded that fluctuation effects on viscoelastic properties completely disappear at around $\chi N < 2 - 3$ for SPs.

### Acknowledgement

Authors thank Mr. Nao Yamada and other staff in Anton Paar Japan for their assistance in SAXS measurements.

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