Nonlinear shear and elongational rheology of entangled poly(propylene carbonate) (PPC) melts having different molecular weights with relatively narrow molecular weight distribution are examined. In shear measurements, the PPCs exhibit a typical shear thinning behavior with stress overshoot at high shear rates. In the shear rate dependence of the steady-state viscosity, the PPCs do not violate the empirical Cox-Merz rule, which is known to be valid for many other entangled polymer melts. In uniaxial elongational measurements, the viscosity growth functions of the PPCs show a weak deviation from the linear viscoelastic (LVE) envelope to the higher side at the high Weissenberg number $Wi_d = \dot{\epsilon} \tau_d$, where $\dot{\epsilon}$ is the elongation rate and $\tau_d$ is the characteristic disengagement time). The steady-state viscosity of the PPCs shows an elongational thinning as a function of $\dot{\epsilon}^{-0.5}$ within an error. These results are similar to some other polymer melts such as polystyrene (PS). In addition, the normalized elongational viscosity growth functions of PPC and PS with a similar entanglement number $Z$, are compared. The PPC exhibits a similar viscosity growth curve to the PS at the same $Wi_d$. This result suggests that the degree of the monomeric friction reduction originated from the stretch/orientation of PPC under fast elongational flow might occur at the same level as PS.

**KEYWORDS:** Poly(propylene carbonate) / Shear rheology / Elongational rheology

1. **INTRODUCTION**

With serious environmental problems caused by petroleum-based common plastics having been reported, biodegradable polymers are promising materials to solve the white pollution. Carbon dioxide (CO$_2$) based polymers which use CO$_2$ as a raw material have been synthesized and studied since 1970s, and they can be used as biodegradable plastics. Among them, poly(propylene carbonate) (PPC), the alternating copolymer of CO$_2$ and propylene oxide, exhibits relatively good properties $^1$-$^7$, which can be widely used in barrier and packaging fields $^8$. With the increase of industrial production volume, the processing of PPC becomes important.

Rheology is a good method to understand the flow and processing behavior of polymers. The linear viscoelasticity (LVE) under small deformation is one of the fundamental properties to characterize the rheological parameters of materials, such as plateau modulus $G_\infty$, zero-shear viscosity $\eta_0$, and so on. Previously, LVE was reported for commercial PPC products $^4$-$^5$, but because of the uncertainty of the samples, i.e., broad molecular weight distribution and unpurified low molecular weight compounds, the basic LVE properties were not consistently reported. Recently, we prepared a series of PPC samples with relatively narrow molecular weight distributions, and reported that $G_\infty$ of PPC is 670 kPa $^6$, which is considerably higher than that reported previously $^5$.

Compared to LVE, it is more difficult for nonlinear viscoelasticity (NLVE) under large and fast deformation to obtain and understand the data. In addition, the responses strongly depend on the deformation manner (e.g., under shear, uniaxial elongation, and so on). Understanding of NLVE properties is also important because it is strongly related to the industrial possessing (e.g., molding, blowing, and so on), where complex large deformations are applied to the materials. As far as we know, only Li et al. $^7$ reported the nonlinear rheology of PPCs with different molecular weights ($i.e., M_n = 26.9-144.6 \text{ kg/mol}$) with relatively broad molecular weight distributions ($i.e., M_n/M_w = 1.92-3.87$) using a capillary rheometer. However, they discussed the obtained data mainly in terms of the processing, but did not carefully discuss from the viewpoint of molecular rheology. In addition, they only reported the results by capillary rheometer, but did not focus on other deformation responses. It has been known that LVE and nonlinear shear rheological properties of entangled polymers are universally determined based on the tube theory $^3$-$^10$, irrespective of chemical species of...
polymers. In contrast, it is recently reported that nonlinear elongational rheological properties depend on polymer species\textsuperscript{11, 12}. Therefore, it is still worth investigating the NLVE properties of PPC under different deformations.

In this paper, we investigate the nonlinear shear and elongational rheological properties of PPC samples having different molecular weights with relatively narrow distribution. The shear and elongational viscosity growth functions of PPCs are obtained at various strain rates, and the strain rate dependence of the steady-state viscosity is discussed. In addition, the uniaxial elongational viscosity data of PPC are directly compared with those of polystyrene (PS), which is one of the most reported polymers for elongational rheology\textsuperscript{11, 13-16}, and the similarities and differences between them are discussed.

2. EXPERIMENTAL

2.1 Materials

Table I shows the samples examined in this study. Five PPC samples having different molecular weights with relatively narrow molecular weight distribution were used. All of them were prepared by precipitation fractionation of a commercial PPC as reported previously\textsuperscript{6}. We have determined the absolute molecular weight by multi-angle light scattering (MALS), and the resultant value is different from that reported in the previous paper according to GPC with PS standards. In this paper, we use the sample codes according to $M_w$ obtained by MALS with asterisks to discriminate them from those used in the previous publication. For most of the samples, linear viscoelasticity was reported in the previous publication, whereas for PPC111k, LVE is reported in Fig. A1 in Appendix. Details of MALS measurements and discussion on LVE will be reported elsewhere\textsuperscript{17}. In addition, we compare the data for the PPC samples with a PS sample reported in the literature\textsuperscript{15}. The molecular characteristics of the PS sample are also shown in Table I.

For the analysis of nonlinear rheological properties, a characteristic disengagement time $\tau_d$ is estimated. If the sample has a monodisperse molecular weight, its terminal relaxation response can be uniquely represented by the weight-average terminal relaxation time $\tau_w$ defined as $\lim_{\omega \to 0} (G'/\omega G'')$. However, the PPC samples in this study have relatively narrow but non-negligible distributions of molecular weight. Thus, in this study, the inverse of $\omega$ at the crosspoint of $G'$ and $G''$ at low frequency is regarded as $\tau_d$, which is more insensitive to the molecular weight distribution.

2.2 Rheological measurements

Small amplitude oscillatory shear measurements were performed by MCR301 (Anton-Paar) rheometer with a strain of 1%. A parallel plate with a diameter of 8 mm was used with a gap value of 1 mm. Angular frequencies $\omega$ of 0.1–100 rad/s were applied at the temperature ranging from 60 °C to 140 °C. The master curves of storage and loss modulus, $G'$ and $G''$, are composed by applying the time-temperature superposition (TTS) with the Williams-Landel-Ferry (WLF) equation\textsuperscript{18}.

Nonlinear shear measurements were conducted at various constant strain rates (i.e., 0.003–100 s$^{-1}$) by MCR301. A cone geometry with a diameter of 8 mm and a cone angle of 1° was used. The measurement of each sample was

| Sample code | $M_w$/MAL$^a$ | $M_w$/GPC$^b$ | $M_w$/M$^b_n$ | $T$ | $\tau_d$ | $c$ |
|-------------|--------------|--------------|--------------|-----|---------|-----|
| PPC344k$^*$ (PPC460k) | 344 | 460 | 1.44 | 100 | 120 |
| PPC253k$^*$ (PPC361k) | 253 | 361 | 1.41 | 100 | 35 |
| PPC158k$^*$ (PPC236k) | 158 | 236 | 1.29 | 70 | 840 |
| PPC111k$^*$ | - | 111 | - | 1.29 | 70 | 140 |
| PPC68.8k$^*$ (PPC105k) | 68.8 | 105 | 1.40 | 70 | 15 |
| PS545k | - | 545 | - | 1.12 | 130 | 2.4 × 10$^4$ |

(a) Determined by GPC-MALS. (b) Determined by GPC with PS standards. (c) Estimated from the reciprocal of $\omega$ at the crosspoint of $G'$ and $G''$ at low frequency. (d) Denoted previously based on $M_w$/GPC in Ref. 6. (e) Prepared newly in this study. (f) The data are taken from the literature in Ref. 15.
successively conducted from low to high shear rates at several temperatures (i.e., 90–120 °C).

Uniaxial elongation measurements were performed with a filament-stretching rheometer, VADER1000 (Rheo Filament). Before measurements, all PPC samples were molded to cylinder specimens with a fixed diameter of 6 mm and a thickness of 2 mm by a hot press at 120–140 °C. After loading a PPC sample on the geometry with 6 mm diameter in VADER, the sample was pre-stretched to a diameter of 2.5–3.5 mm at 120–140 °C to avoid detachment from the plates. Then, the temperature was decreased to 70–100 °C depending on the sample molecular weight of PPCs, and the elongational viscosity measurements were conducted at various constant strain rates (i.e., 0.002–2 s⁻¹).

3. RESULTS AND DISCUSSION

3.1 Linear viscoelasticity

Figure 1 shows a direct comparison of the LVE data of PPC158k* and PS545k. Here, $G'$ and $G''$ in vertical axis are normalized by the plateau modulus $G_0$ (i.e., 670 kPa for PPC158k* and 220 kPa for PS545k), while $\omega$ in the horizontal axis is scaled by multiplying $\tau_e$, which represents the reciprocal of $\omega$ at the crosspoint of $G'$ and $G''$ at high frequency (i.e., $\tau_e = 3.6 \times 10^{-5}$ s for PPC158k* at 100 °C, and 0.12 s for PS545k at 130 °C). The entanglement number $Z = M_e/M_w$ of PPC158k* is calculated as 27 using the entanglement molecular weight $M_e = 5.9$ kg/mol⁶, whereas $Z$ of PS545k is calculated as 30 using $M_e = 18.0$ kg/mol for PS¹⁸. In Fig. 1, the normalized dynamic modulus of PPC158k* and PS545k overlapped well in the range of $1/\tau_e \leq \omega \leq 1/\tau_e$. Note that PPC158k* exhibits a slightly lower $G''$ at $\omega \geq 1/\tau_e$ compared to PS545k, which is probably because of the slight difference in $Z$ as well as $M_e/M_w$.

3.2 Shear rheology

Figure 2 shows the shear viscosity growth functions $\eta'$ against time $t$ at different shear rates $\dot{\gamma}$ for five PPC samples. The two PPC samples with higher molecular weights were measured at 120 °C, while the other three samples were at 100 °C because of the accessible range of the stress in the measurements. At very low $\dot{\gamma}$, $\eta'$ of all PPC samples show a relatively good agreement with the LVE envelope, although the data of some samples is slightly lower in the entire $t$ range. Note that we used a small cone-plate geometry with 8 mm diameter and cone angle of 1°, and hence the absolute value of viscosity might have a margin of error within 30%.

With increasing $\dot{\gamma}$, the viscosity data show a clear shear-thinning behavior with a stress-overshoot before reaching the steady-state. This experimental fact is well-known for many other entangled polymer melts¹⁸,¹⁹, and it is because of the chain orientation in the flow direction²⁰-²². All of the data exhibit a clear steady-state at long $t$ regime even at high $\dot{\gamma}$.

Figure 3 shows the $\eta'$ data for PPC111k* measured at different temperatures. The data were shifted by using the horizontal and vertical shift factors, $a_T$ and $b_T$, for LVE ($a_T = 1.0, 1.8$ and $3.6$, and $b_T = 1.0, 1.03$ and $1.07$, at $100, 95$ and $90$ °C, respectively)⁹, i.e., the horizontal axis is normalized by $a_T$, while the vertical one is by $a_T/b_T$ at the reference temperature $T_r = 100$ °C. The $a_T$ and $b_T$ values used here are those estimated from LVE data, and the details were reported previously⁶. At the same Weissenberg number $Wi_\eta (= \gamma \tau_e)$, the viscosity data at different temperatures overlap well even at high $Wi_\eta$ regime. This result suggests that tTS is applicable for the PPC samples in this study even at the nonlinear regime.

Figure 4 plots the steady-state shear viscosities $\eta(\dot{\gamma})$ obtained from Fig. 2 against $\dot{\gamma}$ for the PPCs at $T_r = 100$ °C. The data for PPC344k* and PPC253k* measured at 120 °C were shifted to those at $T_r = 100$ °C using $a_T (= 0.12)$ and $b_T (= 0.88)$ as we proceeded in Fig. 3. The complex viscosities $\eta'(\omega)$ obtained from dynamic LVE measurements are also plotted against $\omega$ in Fig. 4. At low $\dot{\gamma}$, $\eta(\dot{\gamma})$ depends on the molecular weight of the samples, while at high $\dot{\gamma}$, $\eta(\dot{\gamma})$ for the different PPCs are superimposed on a single line with a slope of $-0.94$. It is known that the empirical Cox-Merz rule ($\eta(\dot{\gamma}) = \eta'(\omega)|_{\omega=\dot{\gamma}}$) is valid to many other entangled polymers¹⁹. It is found that the Cox-Merz rule is not violated for the PPCs. The PPC samples in this study have slightly broad molecular weight distributions (i.e., $M_w/M_n = 1.3–1.4$), and this fact should affect some NLVE properties. In the nonlinear shear experiments, it is known that the Cox-Merz rule holds even for the broad distribution samples¹⁹, and hence
the results in this study are reasonable. At high \( \dot{\gamma} \), \( \eta(\dot{\gamma}) \) of PPCs are slightly lower than the complex viscosity lines. This fact could be due to the edge fracture which is difficult to completely avoid. Snijker et al.\(^{24}\) tested the nonlinear shear experiments of PS and polyisoprene (PI) melts with cone-partitioned-plate geometry to prevent the edge fracture. Nevertheless, both PI and PS show slightly lower viscosities compared to the complex ones at high rates.

### 3.3 Elongation rheology

Figure 5 shows uniaxial elongational viscosity growth function \( \eta_\varepsilon^* \) at different elongation rates \( \dot{\varepsilon} \) for the PPC samples. The two PPC samples with higher molecular weights were measured at 100 °C, while the two samples with lower molecular weights were at 70 °C because of the accessible range of the stress and strain rate values in the measurements. PPC158k* was measured at both 70 °C and 100 °C to cover a wide \( W_\varepsilon \) range, and the data were superimposed at \( T_r = 70 \) °C using \( a_T \) and \( b_T \). Here, the \( a_T \) and \( b_T \)
values estimated from the LVE were applied to the elongational data in the same way as the shear data (cf. Fig. 3). The validity of rTS for the elongational data is confirmed in Fig. A2 in Appendix, as we did for the shear data (cf. Fig. 3).

At very low \( \dot{\varepsilon} \), the \( \eta_{E} \)-data overlap with the LVE envelope for all PPCs except PPC111k\(^{*}\) although the data have a margin of error of 20\%. Note that PPC111k\(^{*}\) exhibits a clear deviation from the LVE envelope, but the detailed reason is unknown. With the increase of \( \dot{\varepsilon} \), the \( \eta_{E} \)-data for all five PPC samples show a slight deviation from the LVE envelope to the higher side. This behavior is qualitatively similar to some entangled linear polymer melts such as PS\(^{11,13-15}\) and poly(methyl methacrylate) (PMMA)\(^{12,25}\), and it is considered by the orientation and stretch of entangled polymer chains\(^{26}\). The viscosity at the steady-state monotonically decreases with increasing \( \dot{\varepsilon} \).

To check the stability of the viscosity in the steady-state, we show the \( \eta_{E} \)-data of the PPC samples as a function of Henky strain in linear scale in Fig. A3 in Appendix. Most of the \( \eta_{E} \)-data for the PPCs reach the steady-state at long \( t \). However, especially at high \( \dot{\varepsilon} \), the range of the steady-state is not wide, and hence the steady-state viscosity \( \eta_{E} \) we estimated has a margin of error within 30\%.

Figure 6 shows a direct comparison of the normalized elongational viscosity growth functions between PPC158k\(^{*}\) and PS545k at the same \( W_{iL} \). Here, the horizontal axis \( t \) is normalized by \( \tau_{e} \), while the vertical axis \( \eta_{E} \) is normalized by \( G_{N} \) and \( \tau_{e} \) (cf. Fig. 1). In Fig. 6, at each \( W_{iL} \), the elongational viscosity growth curve of PPC158k\(^{*}\) is almost overlapped with that of PS545k within an error.

It is known that compared to the nonlinear shear experiments, nonlinear elongational rheology data is more sensitive to the effect of molecular weight distribution. In particular, when the samples contain small amounts of high molecular weight components, they exhibit a significant strain hardening\(^{27,28}\). In contrast, the PPCs in this study do not exhibit such hardening behavior. This is probably because the shape of the distribution is unimodal and also the distribution is not that broad for the PPCs.

Figure 7 shows the elongation rate dependence of normalized steady-state elongational viscosities for PPC and PS. Note that the steady-state elongational viscosity \( \eta_{E}(\dot{\varepsilon}) \) is normalized by \( 3\eta_{0} \) estimated from LVE, while the viscosity data are plotted against \( \dot{\varepsilon} \tau_{e} \). As we can see from Fig. A3 in Appendix, the steady-state range is not that wide especially at high \( \dot{\varepsilon} \), hence \( \eta_{E}(\dot{\varepsilon}) \) has a margin of error within 30\%. In Fig. 7, the normalized \( \eta_{E}(\dot{\varepsilon}) \)-data of the five PPCs show the elongational thinning behavior at \( \dot{\varepsilon} \tau_{e} > 1 \), and they overlapped on a single line with a slope of \(-0.5\) within an error.
original Doi-Edwards tube theory for entangled polymers predicted that the viscosity decreases as a function of $\dot{\varepsilon}^{-1}$ in the range of $1/\tau_R < \dot{\varepsilon} < 1/\tau_R$, where $\tau_R$ represents the Rouse relaxation time. However, similar experimental behavior to PPC, i.e., $\dot{\varepsilon}^{-0.5}$ dependence of $\eta(\dot{\varepsilon})$, is reported for some other well-entangled polymers\textsuperscript{11,13,15}. We can say that the molecular weight distribution of the PPCs in this study does not strongly influence the $\dot{\varepsilon}$ dependence of the steady-state viscosity. The $\eta(\dot{\varepsilon})$ data of PS545k also overlapped with that of PPC158k\textdegree, as we confirmed in Fig. 6.

The original Doi-Edwards model predicts that at the elongation rate higher than $1/\tau_R$, a steep elongation thickening occurs because the polymer chains are highly stretched. In contrast, in experiments, entangled polymer melts such as PS and PMMA do not show such a thickening even at $\dot{\varepsilon} > 1/\tau_R$\textsuperscript{11-13,15}. In fact, the viscosity data of PS545k in Figs. 6 and 7 are ranged in $\dot{\varepsilon} \geq 1/\tau_R$. We can naively think that the data of PPC158k\textdegree are also situated at $\dot{\varepsilon} \geq 1/\tau_R$ since PPC158k\textdegree and PS545k show similar LVE. However, it is probably difficult to uniquely determine $\tau_R$ of the PPC because of the slightly broad $M_w/M_n$. The elongational viscosity data of different polymer melts with the same $Z$ can be discussed by using the maximum stretching ratio $\lambda_{\text{max}}$ of a polymer chain when the molecule is fully stretched\textsuperscript{11,12,15}. For PS $\lambda_{\text{max}}$ is reported as 4.2\textsuperscript{15}, while $\lambda_{\text{max}}$ of PPC in this study is roughly estimated as 6.3 based on the packing length concept\textsuperscript{30}, where the details of the estimation are shown in Appendix. The steady-state stress is expected to scale as $\sigma_{\text{steady}} \propto \lambda_{\text{max}}^2$\textsuperscript{15}. Thus, if the monomeric friction of PPC158k\textdegree and PS545k was comparable, PPC158k\textdegree would exhibit higher viscosity because of its higher $\lambda_{\text{max}}$ at $\dot{\varepsilon} > 1/\tau_R$. Nevertheless, PPC158k\textdegree exhibits a similar viscosity growth curve compared to PS545k at the same $\dot{\varepsilon}$ and also simple elongational thinning behavior, as shown in Figs. 6 and 7.

To explain the elongation thinning behavior of some polymer melts such as PS at $\dot{\varepsilon} > 1/\tau_R$, the concept of the stretch/orientation-induced reduction of monomeric friction (SORF) in fast flow is proposed\textsuperscript{31,32}. Masubuchi et al. successfully explain the experimental elongational data of entangled PS and other polymer melts by considering the SORF in their primitive chain network simulations\textsuperscript{33,34}. One possible reason to explain the results of PPC158k\textdegree is that the SORF might occur for PPC at the same level as PS. Unfortunately, we cannot verify this hypothesis only from the current experimental data. In the near future, we will attempt to estimate the degree of SORF for PPC by measuring the stress relaxation after elongation combined with theoretical and simulation analysis.

Compared to monodisperse PS545k, the PPCs in this study have non-negligible broad $M_w/M_n (= 1.3–1.4)$. At present, we cannot correctly estimate the effect of molecular weight distribution on the elongational viscosity data. In the near future, we will examine the nonlinear rheology of a PS sample, which has the same $Z$ and similar $M_w/M_n$ with PPC158k\textdegree.

4. CONCLUSIONS

Nonlinear shear and elongational rheology of PPCs with different molecular weights are examined. In shear rheology, all five PPC samples exhibit the shear-thinning at high shear rates, and they do not violate the empirical Cox-Merz rule, as known for many other polymers. In elongational rheology, the viscosity growth functions of PPCs show a weak deviation from the LVE envelope, while the steady-state viscosity shows an elongation thinning with the dependence of $\dot{\varepsilon}^{-0.5}$.
when $Wi_d$ is larger than unity. These results are similar to some other polymer melts such as PS. Moreover, the viscosity growth curves of PPC and PS with similar $Z$ are directly compared. The PPC exhibits a similar viscosity growth curve to PS at the same $Wi_d$. This experimental result suggests that the SORF might occur for PPC at the same level as PS. To elucidate this issue, we will examine the elongational rheology of PS with same $Z$ and similar $M_w/M_n$, and also perform the stress relaxation measurements after elongation to estimate the degree of SORF of PPC in the near future.

**APPENDIX**

**A1. LVE of PPC111k**

Figure A1 shows the master curves of $G'$ and $G''$ at $T_r = 100 ^\circ C$ for PPC111k, which is newly prepared in this study. The master curves are constructed by the horizontal and vertical shift of the data at each $T$. We confirmed that the $a_T$ and $b_T$ values applied for PPC111k are consistent with those for the other PPCs as reported previously $^{6}$. 

**A2. Elongational Rheology of PPCs**

Figure A2 shows the elongational viscosity growth functions of PPC111k at different temperatures. The data were shifted by using $a_\varepsilon$ and $b_\varepsilon$ for LVE ($a_\varepsilon = 1, 0.37$ and 0.15, and $b_\varepsilon = 1, 0.97, 0.94$, at 70, 75 and 80 $^\circ C$, respectively) $^{6}$, at $T_r = 70 ^\circ C$, as we did for the shear data (cf. Fig. 3). It can be seen that the tTS holds for PPC111k even at high $Wi_d$.

Figure A3 shows the elongational stress data of the five PPCs against Hencky strain in a linear scale, where the data are the same as those in Fig. 5. In the long $t$ regime, we determine the $\eta_\varepsilon (\varepsilon)$ value at each $\dot{\varepsilon}$.

**A3. Estimation of $C_\infty$ and $\lambda_{\text{max}}$ of PPC**

Based on the packing length concept $^{29}$, the characteristic ratio $C_\infty$ and $\lambda_{\text{max}}$ of PPC are estimated. Note that this estimation is unusual, because the packing length concept is known as universal, but it is still not based on any theoretical background. Nevertheless, we confirmed that the obtained $C_\infty$ and $\lambda_{\text{max}}$ values are in the similar range to the polymers with similar chemical structures, thus the obtained $\lambda_{\text{max}}$ value of PPC is applicable to the discussion in this study.

First, in the packing length concept $^{29}$, the following relation $^{29}$, $p^3 G_N = 12.16 \text{ MPaÅ}^3$, where $p$ represents the packing length, is empirically known for many kinds of polymer melts. For PPC, $G_N = 670 \text{ kPa}^6$ and hence $p$ is estimated as 2.63 Å. From another perspective, $p$ is defined as $p = M/(\langle R^2_0 \rangle \rho N_A)$, where $M$ is the molecular weight, $\langle R^2_0 \rangle$ is the unperturbed mean-square end-to-end distance, $\rho$ is the density of PPC (= 1.26 g/mL) and $N_A$ is the Avogadro’s number. $C_\infty$ is defined as $(\langle R^2_0 \rangle / M)(m_0/l_0^2)$, where $m_0$ is the average molecular weight per backbone bond of length $l_0$, and hence $C_\infty$ is written as $m_0/(l_0^2 \rho p N_A)$. Here, $m_0 = 20.42 \text{ g/mol}$ and $l_0 = 1.19 \text{ Å}$ for PPC $^{35}$, and $C_\infty$ is estimated as 7.22. Using the $C_\infty$ value, the Kuhn segment length $l_K (= C_\infty l_0)$ and Kuhn segment molecular weight $m_K (= C_\infty m_0)$ are calculated as 8.59 Å and 147 g/mol, respectively. Finally, the number of Kuhn segments in an entanglement segment is estimated as $M_e/m_K = 40.1$, and $\lambda_{\text{max}}$ is determined as $\sqrt(M_e/m_K) = 6.3$.
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REFERENCES

1) Luinstra GA, *Polym Rev*, 48, 192 (2008).
2) Luinstra GA, Borchardt E, *Adv Polym Sci*, 245, 29 (2011).
3) Gao F, Zhou Q, Dong Y, Qin Y, Wang X, Xiaojiang Z, Fosong W, *J Polym Res*, 19, 1 (2012).
4) Cao C, Yuan L, Feng L, Wang J, Gu X, *Polym Mater Sci Eng (Chinese)*, 28, 18 (2012).
5) Lin S, Yu W, Wang X, Zhou C, *Ind Eng Chem Res*, 53, 18411 (2014).
6) Yang L, Uneyama T, Masubuchi Y, Doi Y, *Nihon Reoroji Gakkaishi (J Soc Rheol Jpn)*, 49, 267, (2021).
7) Li XH, Meng YZ, Chen GQ, Li RKY, *J Appl Polym Sci*, 94, 711 (2004).
8) Doi M, Edwards SF, “The Theory of Polymer Dynamics”, (1986), Oxford, Clarendon.
9) Likhtman AE, McLeish TCB, *Macromolecules*, 35, 6332 (2002).
10) Auhl D, Ramirez J, Likhtman AE, Chambon P, Fernyhough C, *J Rheol*, 52, 801 (2001).
11) Sridhar T, Acharya M, Nguyen DA, Bhattacharjee PK, *Macromolecules*, 47, 379 (2014).
12) Morelly SL, Palmese L, Watanabe H, Alvarez NJ, *Macromolecules*, 52, 915 (2019).
13) Bach A, Almdal K, Rasmussen HK, Hassager O, *Macromolecules*, 36, 5174 (2003).
14) Laup C, Müller C, Schweizer T, Venerus DC, *Rheol Acta*, 45, 83 (2005).
15) Huang Q, Medtova O, Rasmussen HK, Alvarez NJ, Skov AL, Almdal K, Hassager O, *Macromolecules*, 46, 5026 (2013).
16) Matsumiya Y, Watanabe H, *Macromolecules*, 51, 9710 (2018).
17) Yang L, Uneyama T, Masubuchi Y, Doi Y, *to be submitted*.
18) Ferry JD, “Viscoelastic Properties of Polymers”, 3rd ed, (1980), John Wiley & Sons Inc, New York.
19) Graessley WW. “Polymeric Liquids & Networks: Dynamics and Rheology”, (2008), Garland Science, London and New York.
20) Masubuchi Y, Watanabe H, *ACS Macro Lett*, 3, 1183 (2014).
21) Cao J, Likhtman AE, *ACS Macro Lett*, 4, 1376 (2015).
22) Jeong S, Kim JM, Baig C, *Macromolecules*, 50, 3424 (2017).
23) Cox WP, Merz EH, *J Polym Sci*, 28, 619 (1958).
24) Snijders F, Vlassopoulos D, *J Rheol*, 55, 1167 (2011).
25) Wingstrand SL, Alvarez NJ, Huang Q, Hassager O, *Phys Rev Lett*, 115, 078302 (2015).
26) Wagner MH, Kheirandish S, Hassager O, J Rheol, 49, 1317 (2005).
27) Mueunstedt H, J Rheol, 24, 847 (1980).
28) Minegishi A, Nishioka A, Takahashi T, Masubuchi Y, Takimoto J, Koyama K, Rheol Acta, 40, 329 (2001).
29) Marrucci G, Ianniruberto G, Macromolecules, 37, 3934 (2004).
30) Fetters LJ, Lohse DJ, Richter D, Witten TA, Zirkel A, Macromolecules, 27, 4639 (1994).
31) Ianniruberto G, Brasiello A, Marrucci G, Macromolecules, 45, 8058 (2012).
32) Ianniruberto G, Marrucci G, Masubuchi Y, Macromolecules, 53, 5023 (2020).
33) Yaoita T, Isaki T, Masubuchi Y, Watanabe H, Ianniruberto G, Marrucci G, Macromolecules, 45, 2773 (2012).
34) Masubuchi Y, Matsumiya Y, Watanabe H, Macromolecules, 47, 6768 (2014).
35) To determine $l_0$ of PPC, we assumed that (i) atoms are connected in the trans zigzag configuration with bonding angles of 110° in the main chain, and (ii) the bonding length of C-C and C-O is 1.54 Å and 1.43 Å, respectively.