

Linear Viscoelastic Behaviors of Polybutene-1 Melts with Various Structure Parameters^{*}

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Abstract The effects of weight-average molecular (M_w), molecular weight distribution (MWD), and isotacticity on the linear viscoelastic behavior of polybutene-1 melts are studied. It is observed that the linear viscoelastic region becomes slightly narrower with increasing frequency. In frequency sweeps, the transition of the polymer melts flow from Newtonian flow to power-law flow can be observed. The melts with higher M_w and/or broader MWD, as well as higher isotacticity exhibit higher complex viscosity, zero shear viscosity, viscoelasticity moduli, relaxation modulus, broader transition zone, while lower critical shear rate, non-Newtonian index, and the frequency at which elasticity begins to play an important role. The relationship of zero shear viscosity on M_w has been established, which agrees with the classical power law. Furthermore, it is found that the cross-over frequency decreases with increasing M_w and the cross-over modulus increases with narrowing MWD.

Keywords: Polybutene-1; Molecular weight; Molecular weight distribution; Isotacticity; Linear viscoelastic behaviors.

INTRODUCTION

The discovery of Ziegler-Natta catalysts has been one of the greatest developments in technology for the synthesis of stereoregular polymers in both academy and industry^[1]. Isotactic polybutene-1 (iPB), first synthesized by Natta^[2], is a semi-crystalline plastic^[3]. It possesses a number of outstanding properties including excellent heat-creep resistance, environmental stress cracking resistance, chemical stability, abrasion resistance and plasticity in contrast to the general polyolefins. Therefore, it is honored as the “Golden Plastic” in the world^[4]. It is available for manufacturing pipes, films, and thin plates, especially for hot water pipes^[5]. However, even after more than 50 years from its discovery, and despite its potentials, polybutene-1 (PB-1) is still a relatively unexplored material being produced in limited quantities and has not yet found a large commercial success as compared to the other polyolefins. This is particularly caused by the peculiar polymorphic crystallization behavior and the difficulty of this technology in performing the polymerization of 1-butene^[6–8].

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The effects of the structure parameters (*e.g.*, isotacticity, molecular weight and polydispersity index) on the properties (*e.g.*, stress-strain properties, crystalline behaviors, and polymorphic transformation) of PB-1 have been studied^[9–13]. For example, molecular weight has a strong effect on the stress-strain relations, the flow-induced crystallization, and the formation of phase I at room temperature^[9, 12, 13]. With the increase in isotacticity, both the crystallinity and the mechanical properties increase, the size of the spherulites decreases, and the polymorphic transformation from form II to form I occurs more rapidly^[10, 11].

Rheological studies, specially performed at small-amplitude oscillatory mode, *i.e.* the linear rheological properties, can provide us with the richest information about the macromolecular structure of polymer melts^[14]. The linear viscoelastic properties of monodisperse, polydisperse and well-entangled linear polymers melts have been investigated extensively from both theoretical and experimental points of view^[15–18].

Few papers have dealt with the rheological behaviors of PB-1 melts. Combs *et al.*^[19] studied some poly(1-olefins) melts including PB-1 melts by use of the steady state shear rheological tests and they reported that as the molecular weight increased, the critical shear rate and non-Newtonian index decreased, while the melt viscosity increased. Meanwhile, as the molecular weight distribution (MWD) broadens, the critical shear rate decreases, whereas the normal forces and the non-Newtonian ratio increase. Wang *et al.*^[20] investigated the steady-state and dynamic rheology of a series of poly(1-olefins) melts. They found that the flow curves of the melts depended predominately on MWD, and their empirical relationship developed by Cox and Merz applied to the entire series of poly(1-olefins) at all investigated temperatures. PB-1 samples with different MWD, not modified or modified with nucleating agents, were used as model samples to determine the MWD of linear flexible polymers through the viscoelastic measurements of their melts. The results showed that the evaluation of the molecular weight distribution achieved from rheological data provided well defined M_z/M_w ratios (M_z is viscosity average molecular weight and M_w is the weight-average molecular weight), although M_w/M_n ratios (M_n is the number-average molecular weight) still have large confidence intervals^[21].

The dynamic rheological parameters are greatly influenced by the molecular structure of the polymer melts. So we can have a deeper understanding of the rheological behaviors of polymer melts on molecular level^[22]. However, to the best of our knowledge, there have been no systematic reports of the linear viscoelasticity of *i*PB melts with various structure parameters. Herein, we investigated some fundamental rheological properties of *i*PB melts to catch this gap, and the data reported in this work contain the tests of strain sweep, frequency sweep, temperature sweep, and stress relaxation.

EXPERIMENTAL

Materials and Characterization

To reach meaningful conclusions about the effects of molecular structure on the linear viscoelastic behaviors of *i*PB melts, it is necessary to work with groups of materials that differ in only one molecular characteristic. The samples PB1, PB2, and PB3 were used to examine the effect of M_w on the dynamic rheological behaviors, the samples PB4, PB5, and PB6 were used to study the effect of MWD, and the samples PB2 and PB4 were used to investigate the effect of isotacticity.

Pure raw material PB4 synthesized in our own laboratory and the other *i*PB supplied by Dongfang Hongye Chemical Co. Ltd., were chosen as model polymers for this study. All of them were prepared with conventional heterogeneous Ziegler-Natta catalysts. Some characteristics of these samples are listed in Table 1. The isotacticity of the *i*PB samples was tested by the refluxing diethyl ether method^[23]. The samples were refluxed in diethyl ether in a Soxhlet extraction system for 48 h and then cooled to room temperature to be constant weight. The isotacticity was determined by the ratio of the weight of sample after refluxing to the one before refluxing. The materials do not contain any significant amount of nucleating agents. The accurate values of M_w and MWD (M_w/M_n) of these samples were obtained by gel permeation chromatography (GPC), which was performed on a Waters system equipped with a model 1515 pump, a 2414 refractive index detector. In the test, 1,2,4-trichlorobenzene was used as eluent and monodisperse polystyrene was employed as the standard sample.

Table 1. Structure parameters of polybutene-1 samples

Samples No.	Isotacticity ^c (%)	M_w ^d	M_w/M_n ^d
PB1 ^a	95.43	1220000	6.76
PB2 ^a	98.35	627000	6.25
PB3 ^a	93.27	124000	5.82
PB4 ^b	90.75	552000	7.10
PB5 ^a	95.37	561000	11.97
PB6 ^a	91.25	543000	17.30

^a Polymer supplied by Dongfang Hongye Chemical Co., Ltd;

^b Polymer synthesized in our own laboratory;

^c Measured in diethyl ether in a Soxhlet extraction system for 48 h;

^d M_w , M_w/M_n values were determined by GPC with monodisperse polystyrene as the standard sample.

Sample Preparation

*i*PB resin powders were put into a $L/D = 40$, co-rotating twin-screw lab extruder of CTE20 (Nanjing Corporation Machinery Co. Ltd., China) for extrusion and pelleting. The barrel temperature profile was 160, 180, 190, 200 and 190 °C from hopper to die and the screw speed was set at 60 r/min. During the preparation of the resin pellets, 0.3 wt% antioxidant has been added into the *i*PB powders to prevent thermal-oxidative degradation. Then, the as-obtained *i*PB pellets were dried in vacuum oven at 60 °C for 48 h to remove water. The dried pellets were compression-molded into circular disks with 25 mm in diameter and 1.0 mm thick at 180 °C and 10 MPa for the rheological measurements.

Dynamic Rheological Testing

The linear viscoelastic data were collected by use of a stress-controlled rheometer (DHR-2, TA Instruments, USA) with a parallel-plate configuration. The chosen testing gap was 1.0 mm and the testing temperature was 180 °C. The strain and time sweeps were first performed before dynamic frequency testing to ensure that the frequency sweeps were within the linear viscoelastic and stable region. The strain sweeps were carried out from 0.3% to 300% at the frequency of 1 Hz. Besides, the sample PB2, with medium M_w , was used to study the effect of various frequencies on the rheological properties of *i*PB melts and the frequencies are set from 0.2 Hz to 2.0 Hz. The frequency sweeps covering the range of 600–0.01 rad/s with strain of 1% were performed to investigate the linear viscoelastic behaviors of the polymer melts. The relaxation experiments were performed at 180 °C with the applied strain 3 radians, and the time for relaxation testing was 120 s. All the samples were tested under nitrogen atmosphere to avoid oxidative degradation under testing conditions.

RESULTS AND DISCUSSION

Determination of the Linear Viscoelastic Region

The linear viscoelastic region (LVR) of all *i*PB samples was determined by performing strain sweeps at 180 °C. Figure 1 shows the dependence of the dynamic storage modulus $G'(\omega)$ on the strain of *i*PB melts with various structure parameters. It is evident that there is a region where $G'(\omega)$ is independent of strain amplitude, *i.e.* the LVR, while the modulus decrease dramatically when the strain is beyond 30% for all samples. So we choose the strain of 1% to study the linear viscoelastic behaviors for all *i*PB melts. The modulus increases with an increase of M_w and/or broader MWD at a given strain amplitude, which could be attributed to the larger entanglement density in polymer melts with higher molecular weight or molecular weight tails.

The absolute magnitudes of complex viscosity $\eta^*(\omega)$ and the complex modulus $G^*(\omega)$ were defined as:

$$|\eta^*(\omega)| = \left[\left(\frac{G'}{\omega} \right)^2 + \left(\frac{G''}{\omega} \right)^2 \right]^{1/2} \quad (1)$$

$$|G^*(\omega)| = \left[(G')^2 + (G'')^2 \right]^{1/2} \quad (2)$$

where $G'(\omega)$ is the dynamic storage modulus, $G''(\omega)$ is the dynamic loss modulus, and ω is the dynamic angular frequency. PB2 melts were tested here at various frequencies, and they are depicted in Figs. 2(a) and 2(b), respectively. The linear viscoelastic region becomes narrow slightly with increasing frequency. Furthermore, the decrease in amplitude of $G^*(\omega)$ becomes somewhat pronounced in the non-linear viscoelastic region, *i.e.* the strain beyond 30%, at higher frequencies, which indicates that the structure of polymer melts is more easily destroyed. This phenomenon is evidently related to the characteristic time of molecular structure breakdown and recovery^[24]. The breakdown and recovery of melts structure is a competitive process in the procession of oscillatory shear flow. At lower frequencies, the cycle time is sufficiently enough to allow for the melts structure recovery, and the linear region is longer. While the cycle time is too short, the structure cannot recover at higher frequencies. Consequently, the melt attains its equilibrium state and is earlier to be out of the linear region than that is sheared under low frequency. The similar phenomenon of η^* can be observed from Fig. 2(b).

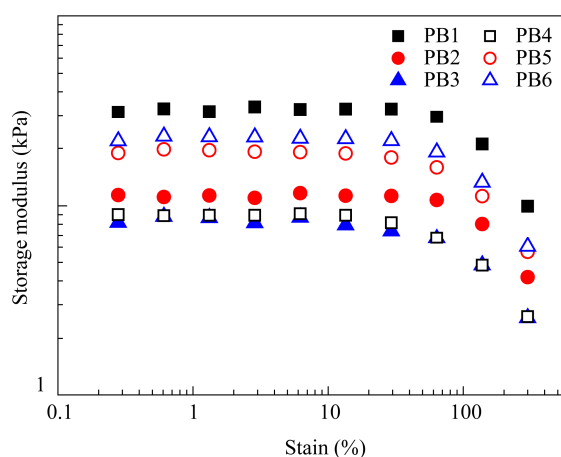


Fig. 1 Storage modulus as a function of strain amplitude for all *iPB* samples with various structure parameters at 1 Hz and 180 °C

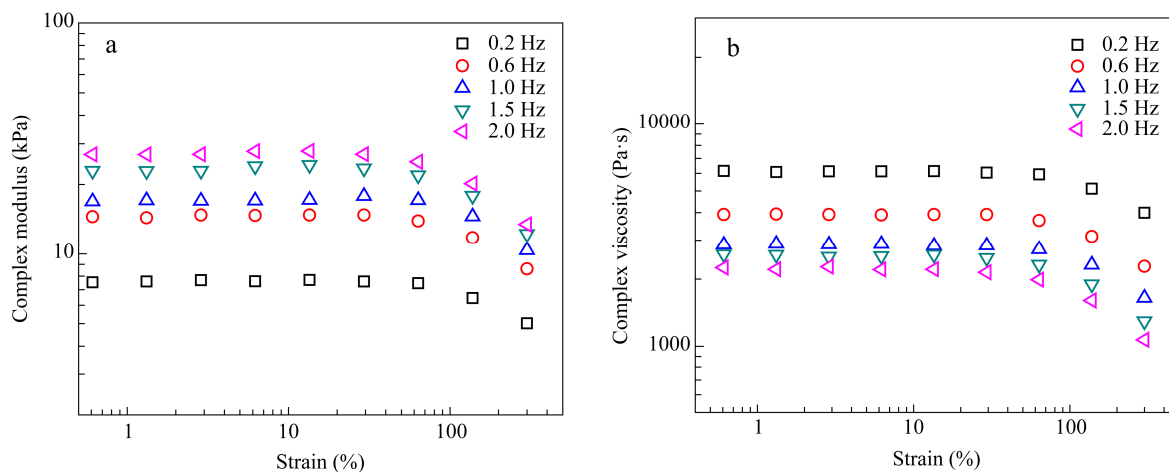


Fig. 2 Complex modulus (a) and complex viscosity (b) as a function of the strain amplitude at various frequencies for PB2 at 180 °C

Frequency Dependence of Dynamic Viscoelasticity

The absolute magnitudes of complex viscosity against angular frequency of all *iPB* samples are shown in Fig. 3. The decreasing of the melts in viscosity with an increase of frequency is attributed to the oscillation-induced change in molecular state, which is often described in terms of entanglement between polymer molecules^[25, 26]. It

can be found that all *i*PB melts show a Newtonian plateau in the low frequency region, and followed by the power-law-like behavior in the high frequency region. This is more distinctive for the samples PB3 and PB6. The Cross model^[27] can be used to express the viscosity properties of the *i*PB samples in the figures:

$$\eta^*(\omega) = \frac{\eta_0}{[1 + (\lambda\omega)^{1-n}]^n} \quad (3)$$

where $\eta^*(\omega)$ is the complex viscosity, η_0 is the zero shear viscosity, λ is the relaxation time, ω is the angle frequency, and n is the non-Newtonian index. The model parameters are summarized in Table 2. According to the plots of $\eta^*-\omega$ and the Cross model parameters, the sample PB1, with higher M_w , shows higher zero shear viscosity, longer relaxation time, broader transition zone between the Newtonian plateau and the power law zone, and a stronger viscosity reduction effect. This can be attributed to the faster relaxation time, higher entanglement density, as well as the easier disentanglement and orientation under stronger shear flow field^[28]. For the samples with various molecular weight distributions, similar results can be obtained for the PB6 with broader MWD. The higher viscosity at low frequencies is due to the high molecular weight tails, which contain more entanglements and make a larger contribution to the melt viscosity. On the other hand, the low molecular weight tails may act as lubricants at high frequencies and reduce the viscosity of polymer melts. Moreover, using these data, we are able to generate the relationship between the zero shear viscosity and molecular weight for *i*PB at 180 °C (Eq. 4).

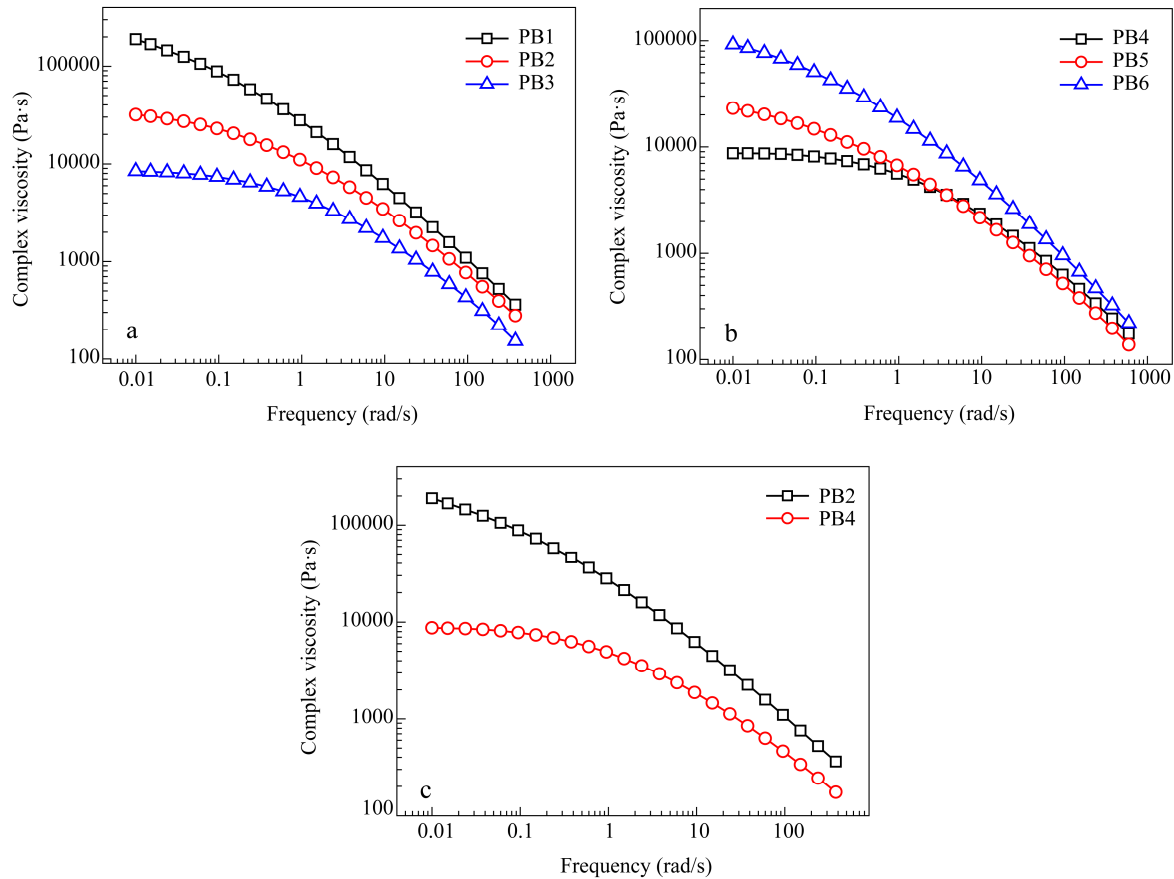


Fig. 3 Variations of complex viscosity with frequency for the *i*PB melts with various structure parameters

$$\eta_0 (\text{Pa}\cdot\text{s}) = 5.7 \times 10^{-16} (M_w)^{3.4} \quad (4)$$

It can be found that the result obtained agree well with the classical power law (3.4–3.6). The pre-exponential factor is different from the literature^[29], which related to the structure of the polyolefin.

Table 2. Model parameters of the polybutene-1 melts at 180 °C

Samples No.	n	λ (s)	η_0 (kPa·s)	ω_x (rad/s)	G_x (kPa)
PB1	0.57	18.20	228.37	0.31	11.17
PB2	0.63	3.40	34.56	3.12	14.05
PB3	0.70	0.64	8.86	12.51	17.00
PB4	0.66	0.51	9.15	12.61	18.33
PB5	0.58	7.04	27.14	3.74	9.43
PB6	0.57	12.10	110.06	0.87	8.03

From the comparison of PB2 and PB4, the molecular weight of PB2 is slightly higher than that of PB4. Such small difference would cause about 54% ($\sim(6.27/5.52)^{3.4}$) increment of viscosity for PB2 as compared to PB4, which cannot account for the great difference in complex viscosity as shown in Fig. 3. Therefore, it would be reasonable to attribute the difference in viscoelasticity between PB2 and PB4 to the difference in the degree of isotacticity.

Another sensitive indicator of rheological differences between materials is the loss angle. The effects of M_w , MWD, and isotacticity on the loss angle are shown in Figs. 4(a), 4(b), and 4(c). As is known, the approach

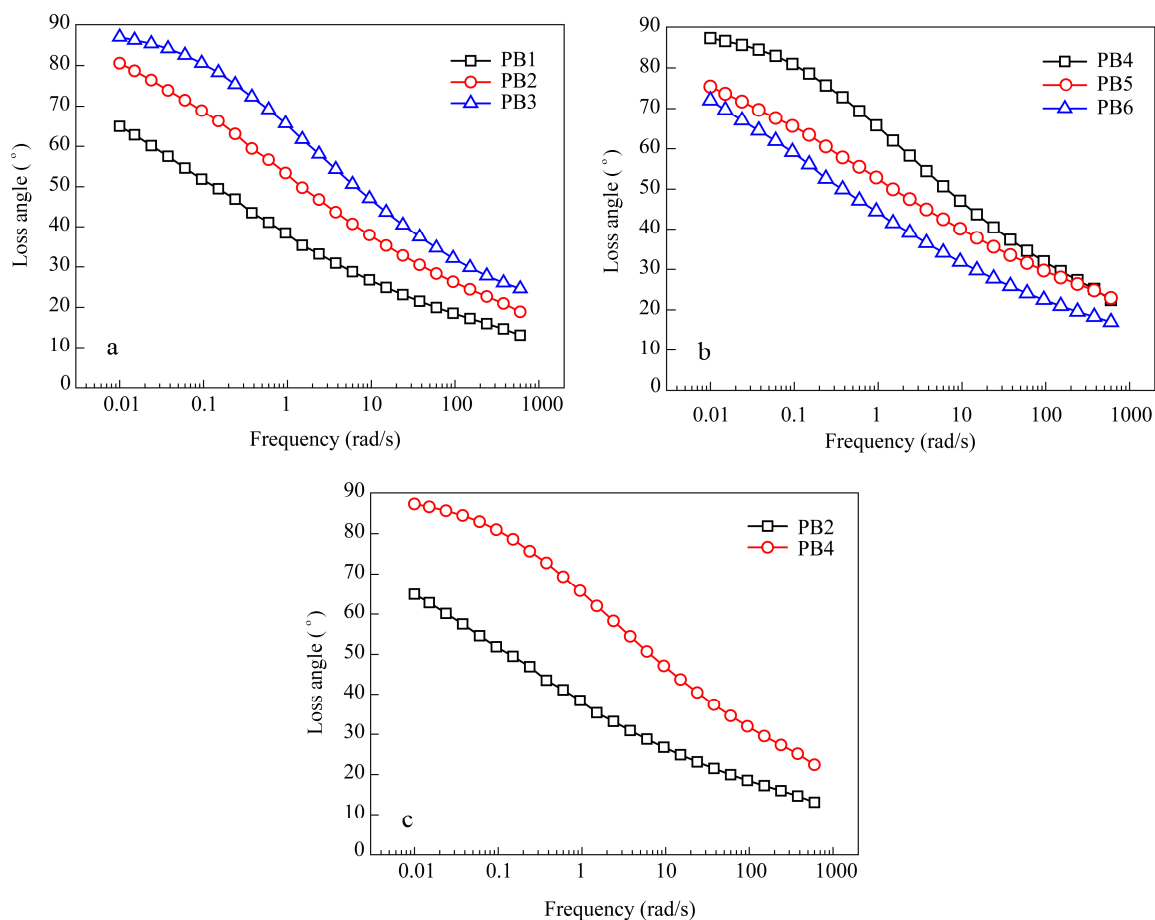


Fig. 4 Effect of molecular structure parameters on loss angle of *i*PB melts

of the loss angle to 90° indicates that the fluids are approaching the terminal zone of Newtonian fluid although it has not yet been reached, while an approach of the loss angle to 0° indicates that the fluid obeys Hooke's Law. It is found that the *i*PB melts with higher M_w , or broadening MWD, or higher chain isotacticity show a lower frequency at which the melts elasticity begins to play an important role.

The linear viscoelastic moduli of the samples at 180°C are shown in Fig. 5. As is well known, $G'(\omega)$ reflects the elastic behavior of polymer fluid which can be viewed as the reflection of the entropy elasticity of the polymer chains. $G''(\omega)$ reveals the viscous behavior of the polymer fluid which can be viewed as the amount of dissipative energy. In the terminal zone, the rheological behavior is dominated by the longest relaxation time, where the $G'(\omega)$ and $G''(\omega)$ of linear polymers follow the well-known frequency dependency^[25]. Although the phenomenon of sample PB1 and PB6 is not very clear, which will be observed at more lower frequencies due the longer relaxation time. For all the samples, $G'(\omega)$ increases more quickly than $G''(\omega)$ with increasing frequency, since most of the energy released during the polymer material deformation translating into elastic deformation. The high molecular weight or high molecular weight tails of samples PB1 and PB6, which lead to the larger viscoelasticity of polymer melts at high frequencies, may be the main source that causes unstable flow occurring more easily under the processing conditions. The viscoelasticity is stronger for the *i*PB melt with higher degree of isotacticity, which can be seen from the comparison of PB2 and PB4.

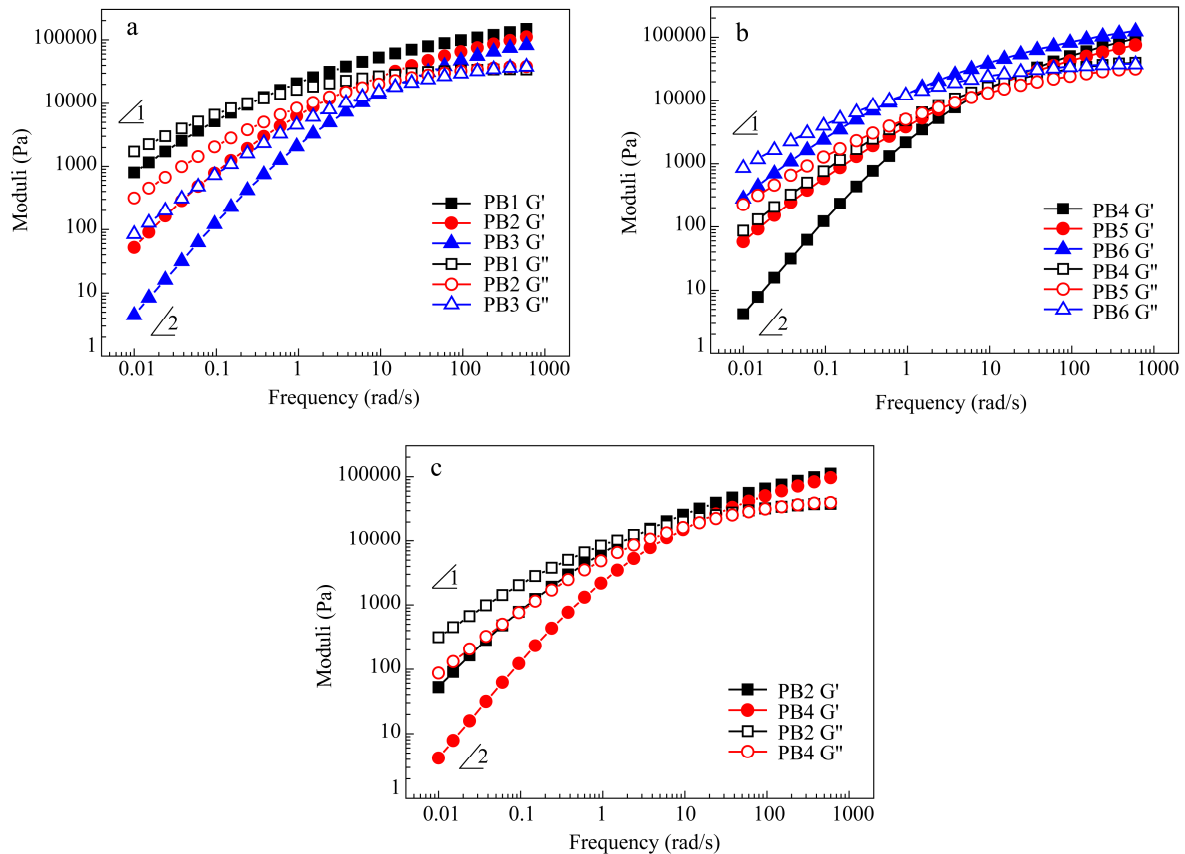


Fig. 5 Viscoelastic moduli as a function of frequency for *i*PB melts with various structure parameters

Within the studied frequency window, all of the samples in the present work show a viscoelastic cross-over point (G_x), at which $G'(\omega)$ equals to $G''(\omega)$. Actually, this point is also the cutoff frequency of viscous-like and elastic-like behaviors of polymer melts. The melts are more viscous than elastic below this frequency, and on the contrary, the melts behave more like a solid (elastic) than a liquid (viscous) when the frequency is above this

value. The values of the G_x and the cross-over frequency (ω_x) of all samples are listed in Table 2. It is found that the G_x rises with the decrease in polydispersity, and this trend agrees with the result that Zeichner *et al.*^[30] obtained from the influence of polymeric polydispersity on polypropylenes, made by Ziegler-Natta catalysis and degraded by chain scission.

On the other hand, the sample PB1 with high molecular weight shows much lower ω_x . When the frequency is lower than ω_x , the molecular chains have enough time to relax and the orientation and disorientation of the molecular chains contribute to $G''(\omega)$ more than $G'(\omega)$. It can be considered that the melt at ω_x reaches a state of equilibrium between the effect of internal friction and orientation. When the frequency is larger than ω_x , because of the insufficient relaxation time for the chains movement, the contribution of the disorientation to the $G''(\omega)$ becomes less pronounced. The increase of $G''(\omega)$ with frequency would be only attributed to the increase of oscillatory shearing frequency. Therefore, the polymer melts with higher molecular weight will have lower ω_x ^[31]. Moreover, the corresponding reptation time, τ_r , determined from the reciprocal of the ω_x , is longer for PB1, followed by PB2 and PB3. According to Doi-Edwards^[17], the reptation time, corresponding to the longest relaxation time of polymer chains, is directly proportional to the monomeric friction coefficient and somewhat related to the molecular weight. In addition, it is found that the ω_x of PB2 is lower than that of PB4, which means that the *i*PB with higher degree of isotacticity possesses longer relaxation time in the melt state.

The loss factor, $\tan\delta = G''/G'$, indicating the recovery characteristics of the melts after deformation, is shown in Fig. 6. There are pronounced differences between the $\tan\delta$ of polymer melts in the lower frequency region, where the values of $\tan\delta$ are larger than 1. This means that $G''(\omega)$ is larger than $G'(\omega)$, and the polymer

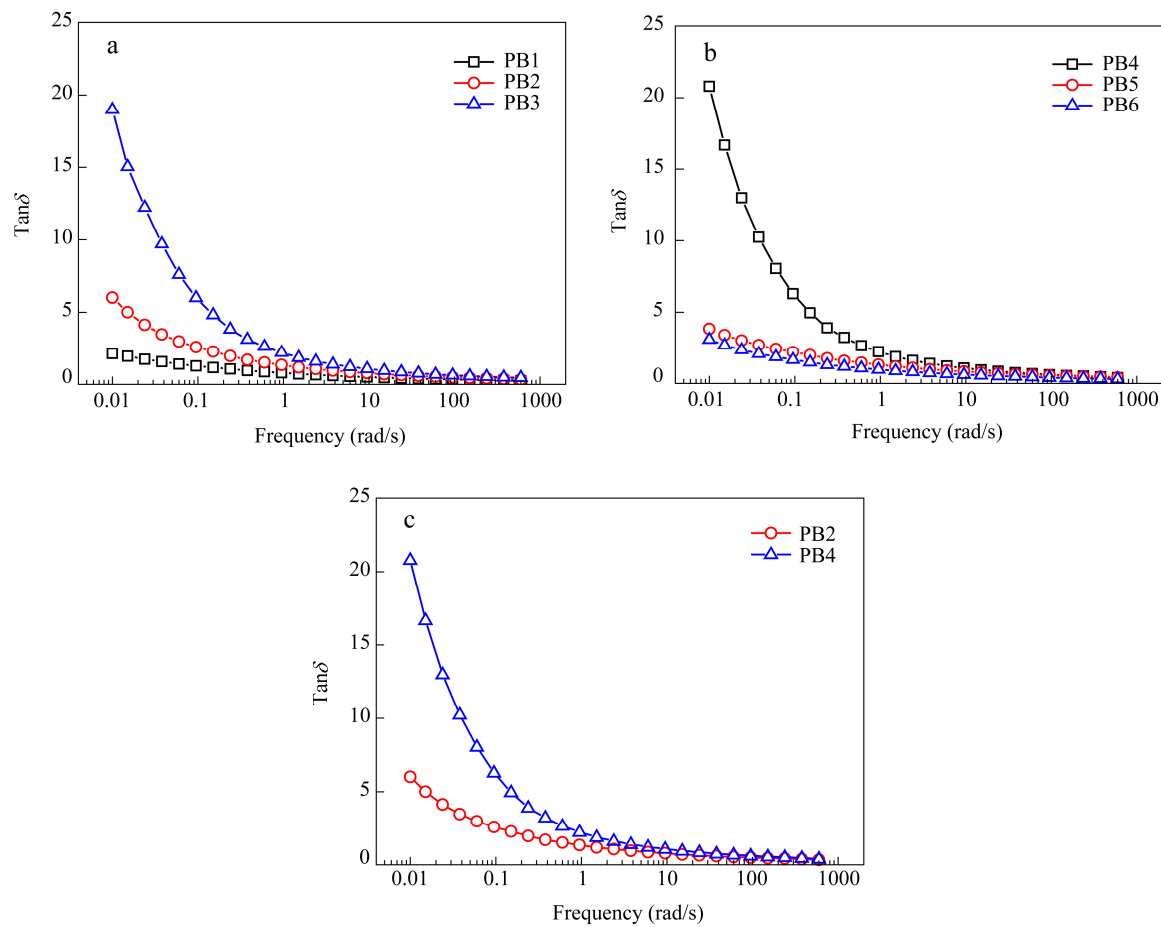


Fig. 6 The loss factor as a function of frequency for *i*PB melts with various structure parameters

melts will recover very slowly after being stressed. With M_w decreasing, or MWD narrowing, or the degree of isotacticity decreasing, the $\tan\delta$ increases at a fixed frequency, indicating the melts behaves more as a viscous fluid than as an elastic solid. Meanwhile, the $\tan\delta$ of these melts drops considerably with frequency increasing owing to the larger incline of $G'(\omega)$ than that of $G''(\omega)$. The difference of the $\tan\delta$ between the melts is very small and nearly independent of angular frequency at high frequencies.

Temperature Effect on the Modulus

The temperature dependence of the viscoelastic moduli of *i*PB melts is shown in Fig. 7. It is found that the temperature dependency of elasticity is more sensitive than that of viscosity from the evidence that the reduction amplitude of $G'(\omega)$ is larger than that of $G''(\omega)$ when the temperature increases from 140 °C to 200 °C. It is also evident that increasing the processing temperature is a practicable way to improve the flow properties of the polymers. In addition, the decline of the viscoelastic moduli with increasing temperature shows us that the moduli of *i*PB melts with lower M_w , as well as the melts of narrower MWD and lower isotacticity, exhibit more dependence on temperature under the dynamic temperature sweep.

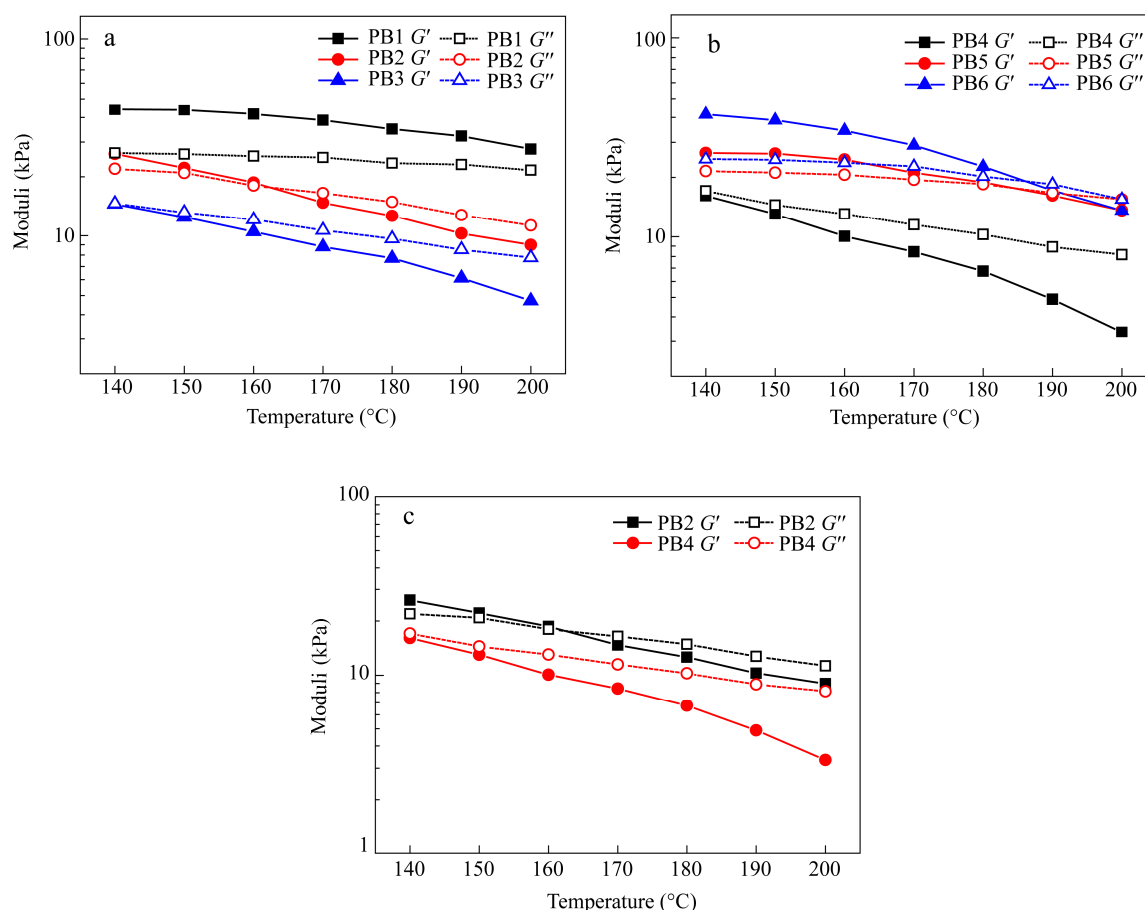


Fig. 7 Storage modulus and loss modulus as a function of temperature for *i*PB melts with various structure parameters

Relaxation Behavior

Figure 8 shows the relaxation modulus $G(t)$ of *i*PB melts versus time data. Generally, there are two zones in the stress relaxation plot, *i.e.*, the plateau zone and terminal zone. In the plateau zone, more time is required for the polymer entanglement network to be disentangled, even though the plateau zone is not obvious for all of the samples in this study. When enough time has passed, the macromolecular chains start to disentangle from the

network, and the concentration of un-relaxed chains becomes less, which promotes a further drop of modulus in the terminal zone^[32]. In general, samples with high molecular weight or high molecular weight tails as well as with higher isotacticity, show a little slower relaxation rate than others in each group, which is evident from the slope of the curves. The relaxation experiment results agree well with the results obtained from the characteristic relaxation time, $1/\omega_x$, which has been discussed previously.

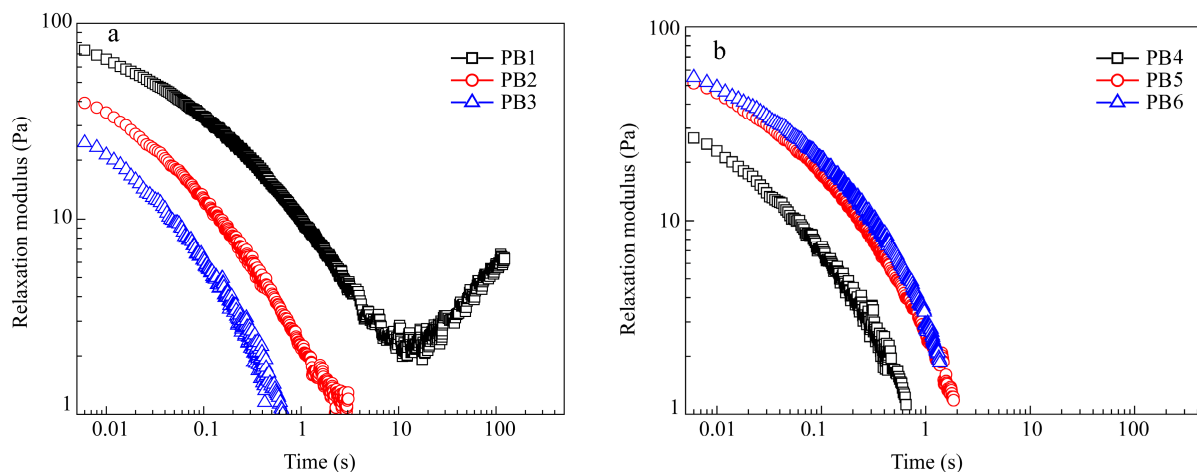


Fig. 8 The plots of relaxation modulus versus time for *iPB* with different weight-average molecular weight (a) and molecular weight distribution (b)

CONCLUSIONS

The rheological behaviors of *iPB* melts with various structure parameters including varied M_w , MWD, and isotacticity are studied by dynamic rheology testing. It is found that the linear viscoelasticity region becomes narrower slightly and the reduction amplitude of $G^*(\omega)$ and $\eta^*(\omega)$ becomes somewhat pronounced in the non-linear viscoelastic region with increasing frequency for the *iPB* melt with medium M_w , which can be explained from the perspective of molecular structure in the melt state.

With increasing M_w or broadening MWD, the melts viscosity, viscoelastic moduli, and transition zone from Newtonian flow to power-law flow increase. Meanwhile, the critical shear rate, non-Newtonian index, loss factor, relaxation rate, the temperature dependence of viscoelasticity, as well as the frequency at which elasticity begins to play an important role tend to be lower or weaker. The relationship of zero shear viscosity on M_w has been established, which agrees with the classical power law. The above-mentioned rheological behaviors of the PB-1 melt with higher M_w can be attributed to the higher entanglement density and longer relaxation time of molecular chains, while the behaviors of the PB-1 melt with broader MWD may be due to the coexistence of the entanglement of the high molecular weight tails and the plasticity effect of the low molecular weight tails. It is also observed that ω_x decreases with M_w increasing, and G_x has a negative correlation with MWD. Moreover, the PB-1 sample with lower isotacticity, shows lower melt viscosity and moduli, narrower transition zone from Newtonian flow to power-law flow, but higher critical shear rate, non-Newtonian index, loss factor, relaxation rate, stronger temperature dependence of viscoelasticity, and the higher frequency where elasticity begins to play an important role, which may be attributed to the stronger ability of chains movement in the melt state under the flow field. Furthermore, it is evident that the dependency of elasticity on temperature is more sensitive than that of viscosity for all PB-1 melts in the temperature sweeps.

REFERENCES

- 1 Jiang, X.B. and He, A.H., *Polym. Int.*, 2014, 63(2): 179
- 2 Natta, G., *J. Polym. Sci.*, 1955, 16(82): 143
- 3 Lee, M.S. and Chen, S.A., *J. Polym. Res.*, 1996, 3(4): 235
- 4 Foglia, A.J., *Appl. Polym. Symposia*, 1969, 11: 1
- 5 Takashi, Y., Masahiko, K. and Hideki, I., 1988, *European Pat.*, 294767 A1
- 6 Marega, C. and Marigo, A., *Mater. Eng.*, 2002, 13(3): 337
- 7 Lucaini, L., Seppälä, J. and Lofgren, B., *Prog. Polym. Sci.*, 1988, 13(1): 37
- 8 Huang, B.C., Zheng, B.Y., Yao, W., Ma, S.Y., Shao, H.F. and Cui, Y.Y., 2007, *C.N. Pat.*, 101020728A
- 9 Rakus, J.P., Mason, Charles D. and Schaffhauser, R.J., *J. Polym. Sci., Polym. Lett. Ed.*, 1969, 7(8): 591
- 10 Shao, H.F., Jiang, D.X., Zhang, M.M., Yao, W. and Huang, B.C., *J. Polym. Res.*, 2012, 19(8):1
- 11 Shao, H.F., Yao, W., Huang, B.C., Zhao, Y.X., *J. Polym. Eng.*, 2009, 29(6): 341
- 12 He, A.H., Xu, C S., Shao, H.F., Yao, W. and Huang, B.C., *Polym. Degrad. Stab.*, 2010, 95(9): 1443
- 13 Jimmy, B. and Peter, V.P., *Polymer*, 2006, 47(16): 5871
- 14 Yang, M.B., Yang, W., Yu, Q.S., Li, Z.M., Feng, J.M. and Xie, B.H., *Proceeding to the seminar on China Application of Engineering Plastics Processing*, 2002
- 15 McLeish, T.C.B., *Adv. Phys.*, 2002, 51(6): 1379
- 16 Wasserman, S.H. and Graessley, W.W., *J. Rheol.*, 1992, 36(4): 543
- 17 Doi, M. and Edwards, S.F., “*The theory of polymer dynamics*”, Oxford Press, New York, 1986
- 18 Cloizeaux, D.J., *Europhys. Lett.*, 1988, 5(5): 437
- 19 Combs, R.L., Slonaker, D.F. and Coover, H.W., *J. Appl. Polym. Sci.*, 1969, 13(3): 519
- 20 Wang, J.S., Knox, J.R. and Porter, R.S., *J. Polym. Sci., Polym. Phys. Ed.*, 1978, 16(10): 1709
- 21 Nobile, M.R., Cocchini, F. and Sterzynski, T., *13th Proceedings of the International Congress on Rheology* (Cambridge, United Kingdom), 2000, 1: 254
- 22 Xu, J.T., Xu, X.R., Zheng, Q., Feng, L.X. and Chen, W., *Eur. Polym. J.*, 2002, 38(2): 365
- 23 Higgins, T.L. and Klingensmith, G.B., 1986, *U.S., Pat.*, H179
- 24 Isayev, A.I. and Fan, X.Y., *J. Mater. Sci.*, 1994, 29(11): 2931
- 25 Han, C.D., “*Rheology in polymer processing*”, Academic Press, New York, 1976
- 26 Dealy, J.M. and Wissbrun, K.F., “*Melt rheology and its role in plastics processing*”, New York, VNR, 1990
- 27 Cross, M.M., *J. Appl. Polym. Sci.*, 1969, 13(4): 765
- 28 Wu, Q.Y. and Wu, J.A., “*Polymer rheology*”(in Chinese), Higher Education Press, Beijing, 2002, p.51
- 29 Wang, J.S., Knox, J.R. and Porter, R.S., *J. Polym. Sci., Polym. Phys. Ed.*, 1978, 16(10): 1709
- 30 Zeichner, G.R. and Macosko, C.W., *Macromol. Symp.*, 1982, 861
- 31 Zhai, Y.M., Yang, W., Wang, Y., Xie, B.H. and Yang, M.B., *Polym. Mater. Sci. Eng.* (in Chinese), 2010, 26(1): 88
- 32 Shao, H.F., Yu, Q.H., Xiao, P., Yao, W. and Huang, B.C., *Polym. Sci., Ser. A+*, 2012, 54(9): 760