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Rheological and Dielectric Behavior of Polyisoprene
under Pressurized Carbon Dioxide

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For a well-entangled polyisoprene (PI; molecular weight = 260k) equilibrated under pressurized carbon dioxide (CO₂) at 25 °C, linear viscoelastic and dielectric data, respectively, were measured with a stress-controlled rheometer and a dielectric bridge being equipped with respective high-pressure cells. The viscoelastic and dielectric data shifted to higher frequencies with increasing CO₂ pressure, indicating that the pressurized CO₂ dissolved into PI thereby accelerating the global motion of PI. For those data at various CO₂ pressure, time-CO₂ pressure superposition held well and a single master curve was obtained, and the horizontal/vertical shift factors were consistent for the viscoelastic and dielectric data. These results indicated that the dissolved CO₂ behaved just as an ordinal solvent to accelerate the global motion of PI as in ordinary solutions. In fact, the dynamic tube dilation (DTD) relationship between the viscoelastic and dielectric data, known to be valid for ordinary solutions/bulk of linear PI, was found to work also the PI/CO₂ system, which confirmed the simple solvent role of the pressurized CO₂ for the global motion of PI. Thus, the knowledge for ordinary polymer solutions would work for processing of polymer/CO₂ systems.

Key Words: Pressurized carbon dioxide / Polyisoprene / Rheological and dielectric behavior

1. INTRODUCTION

Carbon dioxide (CO₂) is widely utilized in the field of polymer processing.^{1,2)} Pressurized CO₂ is considerably soluble in a variety of polymers and decreases their glass transition temperature (T_g). For a practical purpose, it is important to know the polymer rheology under pressurized CO₂. In fact, rheological measurements have been performed with pressure cells to reveal non-Newtonian flow behavior of polymers under fast shear.³⁻⁷⁾ It is also desired to investigate an effect of CO₂ on the polymer dynamics at equilibrium, but just a few set of linear viscoelastic data under pressurized CO₂ (for low density polyethylene⁸⁻¹⁰⁾ and polypropylene^{9,10)}) has been reported due to the technical difficulties.⁸⁻¹⁰⁾ Those linear viscoelastic data were obtained with a stress rheometer equipped with a high-pressure cell, and only a limited aspect of the polymer dynamics has been elucidated because the magnetic driving mechanism of the cells works just in a rather narrow range of frequency.

For full investigation of the global dynamics of polymers governing the terminal relaxation/flow behavior at equilibrium, we recently conducted a dielectric test on polyisoprene

(PI) of a moderate molecular weight ($M_w = 2.0 \times 10^4$) under pressurized CO₂ up to the pressure of $P_{CO_2} = 10$ MPa at 65 °C (which included the supercritical state of CO₂) and at frequencies ranging from 1 Hz to 10 MHz.¹¹⁾ PI has the type-A dipole parallel along the chain backbone and thus the dielectric data (easily measured even in a high pressure cell) reflected the end-to-end vector fluctuation of the PI chain, *i.e.*, the motion over the maximum length scale of the chain. This motion was accelerated while its mode distribution was not affected by pressurized/dissolved CO₂ even for the case of CO₂ in the supercritical state. This result suggested that CO₂ behaves as an ordinary solvent (or plasticizer) for the global dynamics of PI.

Even though the above dielectric results provided us a new insight for the role of the pressurized CO₂ in the global dynamics of PI, it is still early to conclude that CO₂ behaves as an ordinary solvent in all aspects. In fact, the effect of CO₂ on the *local segmental dynamics* (acceleration without mode broadening) is known to be different from that of ordinary solvents (acceleration with mode broadening), and this difference is attributable to very rapid motion of the CO₂ molecules.¹²⁾ Thus, it is desired to test if CO₂ perfectly behaves as an ordinary solvent for the slow, global dynamics of polymers.

For this purpose, we can utilize a difference between the slow viscoelastic and dielectric relaxation processes of

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linear PI chains. These processes detect the same thermal motion of the chain in a different way and thus the frequency dependence (relaxation mode distribution) is totally different for the complex modulus G^* and complex dielectric constant ε^* .¹³ The mode distributions of G^* and ε^* are sensitive and insensitive, respectively, to the entanglement. This difference results from the difference in the fundamental molecular functions of the viscoelastic and dielectric relaxation, the orientation function and local correlation function, the former being an isochronal, second-order average of the bond vectors $\mathbf{u}$ of the stress sustaining unit while the latter being the non-isochronal second-order average (average of $\mathbf{u}$ at different times).¹³ Thus, the comparison of the viscoelastic and dielectric data for PI/CO₂ systems would enable us to experimentally test if CO₂ really behaves as an ordinary solvent for the slow, global dynamics of PI.

This paper reports the results of this test. Because of the difference between the fundamental molecular functions of the viscoelastic and dielectric relaxation, there is no universal relationship between viscoelastic and dielectric data of PI having the type-A dipoles. However, for entangled linear PI, a simple relationship reflecting the finite lifetime of entanglements is known to hold between the normalized viscoelastic and dielectric relaxation functions.^{13,14} Thus, we tested the validity of this relationship for the PI/CO₂ system. The relationship did hold for the PI/CO₂ system, confirming that CO₂ behaves as an ordinary solvent/plasticizer for the global motion of entangled polymers. The details of this result are presented below.

2. EXPERIMENTAL

2.1 Material

Polyisoprene (PI260k, $M_w = 2.6 \times 10^5$, $M_w/M_n = 1.7$) was kindly supplied from Sumitomo Rubber Industries, Co., and was used as received. Carbon dioxide (CO₂) was purchased from Kyoto Teisan Co. Ltd. and used as received.

2.2 Dielectric Measurement

The setup and the protocol of the dielectric measurements under pressurized CO₂ were basically the same as those reported in our previous studies.^{11,12} The sample (PI260k) was charged between main and counter electrodes made of sintered metal (the former having a guard electrode) placed in a high-pressure jacket, exposed to CO₂ having the pressure P_{CO_2} /MPa = 0 (atmospheric ambient pressure), 2, 4, 6, 8, and 10 and fully equilibrated (as monitored through lack of the time dependent change of the dielectric data), and then subjected to

the measurement at each P_{CO_2} . All these operations were made at 25 °C, and the measurement was made in the increasing order of P_{CO_2} . The vapor pressure of CO₂ at 25 °C is 6.8 MPa.¹⁵ Therefore, CO₂ was in gaseous state at $P_{\text{CO}_2} \leq 6$ MPa while in liquid state at $P_{\text{CO}_2} = 8$ and 10 MPa.

The dielectric signal was measured with an impedance analyzer combined with a dielectric interface (1260/1296, Solartron) in a range of the angular frequency ω between 10^{-2} s^{-1} to 10^4 s^{-1} . Differing from the previous study, we utilized a CO₂ pressure controlling system, a syringe-type pump (260D, Isco) with flow panel, which was shared with the rheological setup explained later. This system enabled a little better control of the CO₂ pressure compared to the previous setup^{11,12} (having direct connection to a CO₂ tank through a regulator).

2.3 Linear Viscoelastic Measurement

A stress-controlled rheometer (MCR-301, Anton Paar) equipped with a high-pressure cell unit (Anton Paar) was employed for the linear viscoelastic measurements. CO₂ cylinder with a gas regulator was connected to a syringe-type pump (260D, Isco) equipped with a flow control panel, which allowed the pressured CO₂ gas to be introduced to the high-pressure cell. Figure 1 illustrates the measurement setup including this cell. The sealed cell has a gas inlet that allows CO₂ gas to be introduced. The sample is placed between the lower fixture (25mm ϕ) and the upper plate-type (20mm ϕ) fixture, the latter being made of a sintered metal and having a magnet on its top part. The upper fixture was driven by the outside magnet to apply a commanded stress (torque) to the specimen, and the corresponding strain was detected. With this driving mechanism, the measurements could not be well conducted at high angular frequencies ω (where the

Fig. 1. Schematic illustration of viscoelastic measurement setup including the high-pressure cell.

upper fixture cannot follow the outside magnet to exhibit a mechanical delay) and at low ω (where the friction disturbed an accurate application of the torque), as reported previously.⁸⁾ Thus, we utilized an ordinary, directly-driven strain-controlled rheometer (ARES, Rheometrics) to calibrate/correct the high-pressure setup of the stress-controlled rheometer with the previous method⁸⁾ (the calibration/correction being made for the inertia/friction of the upper fixture and the difference of the upper and lower fixture diameters) and specify the range of ω ($= 10^{-1} \text{ s}^{-1} - 10 \text{ s}^{-1}$) where we could reliably utilize the high-pressure setup. The data of storage and loss moduli, G' and G'' , obtained after the calibration/correction are believed to be acceptably accurate (with uncertainty smaller than 30 %, as judged from reproducibility in several independent runs) and the best available data at this moment.

The measurement was conducted for PI260k under CO_2 in the high-pressure setup at 25 °C. The CO_2 pressure

was chosen to be $P_{\text{CO}_2}/\text{MPa} = 0, 2, 4, 6, 8$, and 10, and the equilibration of PI260k (saturation with CO_2) at each P_{CO_2} was confirmed from lack of time-dependent change of the moduli (at $\omega = 6.28 \text{ s}^{-1}$) for the exposure time $\geq 15 \text{ h}$. The experimental run at each equilibrated state was made in the order of increasing P_{CO_2} .

3. RESULTS

3.1 Dielectric Behavior of PI260k under pressurized CO_2

Figures 2(a) and 2(b), respectively, show the angular frequency (ω) dependence of the decrease of dielectric constant, $\varepsilon_0 - \varepsilon'(\omega)$ with $\varepsilon_0 = \varepsilon'(0)$, and the dielectric loss, $\varepsilon''(\omega)$, of PI260k equilibrated under various P_{CO_2} at 25 °C. (In the phenomenological framework of linear stimulus-response theory, $\varepsilon_0 - \varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are analogous to the viscoelastic G' and G'' , respectively, and expressed in terms

Fig. 2. Frequency dependence of (a) decrease of dielectric constant, $\varepsilon_0 - \varepsilon'$, and (b) dielectric loss, ε'' , measured for PI260k equilibrated under various P_{CO_2} at 25 °C. Panel (c) shows the time- CO_2 pressure superposed master curve of the $\varepsilon_0 - \varepsilon'$ and ε'' data. Solid curves indicate $\varepsilon_0 - \varepsilon'$ and ε'' recalculated from eq.8 with the normalized dielectric intensities g_p and dielectric relaxation times τ_p therein being determined from an iterative fitting method.²¹⁾ For more details, see text.

of the relaxation spectrum.¹³⁾ CO₂ is a non-polar molecule and is dielectrically inert at ω examined. Hence the dielectric relaxation observed here is exclusively attributed to the global motion of well entangled PI260k chains. This relaxation shifts toward higher ω and its intensity decreases with increasing P_{CO_2} up to 6 MPa, which indicates that the pressurized CO₂ dissolves in PI260k to give the plasticization and dilution effects on the global motion at those P_{CO_2} . A similar result was noted also in our previous study.¹¹⁾ In contrast, at $P_{\text{CO}_2} \geq 8$ MPa exceeding the vapor pressure of CO₂ at 25 °C (= 6.8 MPa¹⁵⁾), the $\varepsilon_0 - \varepsilon'$ and ε'' data become insensitive to P_{CO_2} possibly because the dissolution of CO₂ into PI was saturated due to liquefaction of CO₂.

Concerning this behavior at high P_{CO_2} , a reviewer of this paper suggested a possibility of liquid-liquid phase separation of PI being equilibrated with liquefied CO₂. This phase separation should unavoidably lead to coexistence of slow and fast PI chains (in PI-rich and PI-poor phases, respectively). Nevertheless, no dielectric mode broadening attributable to this coexistence is observed in Figure 2, which indicates that our PI equilibrated with liquefied CO₂ exhibited negligible liquid-liquid phase separation and stayed in uniform, one phase state even under the high P_{CO_2} examined.

Figure 2(c) shows the time- P_{CO_2} superposed master curves, $(\varepsilon_0 - \varepsilon')/b_{p,e}$ and $\varepsilon''/b_{p,e}$ as a function of $\omega a_{p,e}/s^{-1}$. The shift factors, $a_{p,e}$ and $b_{p,e}$ are shown later in Figures 4(a) and 4(b). The excellent superposition seen in Figure 2(c) indicates that CO₂ does not affect the dielectric relaxation mode distribution and thus has no influence for the mode of chain motion (relaxation mechanism) of the entangled PI260k. A similar result was noted in our previous study.¹¹⁾

3.2 Viscoelastic behavior of PI260k at pressurized CO₂

Figures 3(a) and 3(b), respectively, show storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, of PI260k equilibrated under various P_{CO_2} at 25 °C. The G' and G'' curves shift toward higher frequencies with increasing P_{CO_2} up to 6 MPa, which reflects the plasticization and dilution effects of unliquefied CO₂. For $P_{\text{CO}_2} \geq 8$ MPa, the G' and G'' curves become almost insensitive to P_{CO_2} due to saturation of dissolved CO₂ concentration on liquefaction of CO₂. These features are qualitatively similar to those seen for the dielectric data (Figures 2(a) and 2(b)).

For the G' and G'' data, we tested the time-CO₂ pressure superposition. The results are shown in Figure 3(c). Clearly, the superposition holds for those data, again indicating that CO₂ does not affect the mode of chain motion (relaxation mechanism) of the entangled PI260k. The shift factors for the modulus data, $a_{p,G}$ and $b_{p,G}$ are compared with the dielectric shift factors, $a_{p,e}$ and $b_{p,e}$, later in Figures 4(a) and 4(b).

4. DISCUSSION

4.1 Shift Factors

Figures 4(a) and 4(b), respectively, show the dielectric/viscoelastic horizontal shift factors, $a_{p,e}$ and $a_{p,G}$, and dielectric/viscoelastic vertical shift factors, $b_{p,e}$ and $b_{p,G}$, utilized in Figures 2(c) and 3(c). These shift factors strongly depend on P_{CO_2} in the range of $P_{\text{CO}_2} < 6$ MPa (where CO₂ has not liquefied) while the P_{CO_2} dependence becomes weak for $P_{\text{CO}_2} \geq 8$ MPa (where liquefaction occurs), as already noted in Figures 2 and 3.

The dielectric, horizontal and vertical shift factors, a_p and b_p , respectively are related to the acceleration of the PI chain

Fig. 3. Linear viscoelastic storage and loss moduli, (a) G' and (b) G'' , measured for PI260k equilibrated under various P_{CO_2} at 25 °C. Panel (c) shows the time-CO₂ pressure master curve of the moduli data. Dashed and solid curves in panel (c) show G' and G'' calculated from the dielectric data (Figure 2) through the full-DTD relationship, eq 6.

motion and dilution (decrease of the PI concentration) on the increase of P_{CO_2} , as noted in our previous work.¹¹⁾ The viscoelastic horizontal shift factor $a_{p,G}$ agrees well with the dielectric $a_{p,\varepsilon}$, indicating that the viscoelastic and dielectric data commonly detect the accelerated PI chain motion under CO_2 . On the other hand, the dielectric/viscoelastic vertical shift factors, $b_{p,\varepsilon}$ and $b_{p,G}$, are considerably different from each other. This difference can be related to the entanglement, as discussed below.

The dielectric $b_{p,\varepsilon}$ factor is directly related to the concentration/volume fraction of PI in the PI/ CO_2 system, as clearly noted from the expression of the dielectric intensity $\Delta\varepsilon$,^{16,17)}

$$\Delta\varepsilon = Fg\nu \frac{p^2}{3k_B T} \quad (1)$$

Here, F is Onsager factor having a value of the order of unity, p is the total dipole moment of a molecule (of the PI chain), k_B is the Boltzmann constant, T is the absolute temperature, and ν is the number density of the dipoles. g is the Kirkwood-Fröhlich factor that represents motional correlation of the dipoles. Since the dielectric mode distribution of PI260k does not change with P_{CO_2} (cf. Figure 2), the dielectric vertical shift factor $b_{p,\varepsilon}$ is identical to a ratio of the of the dielectric intensity $\Delta\varepsilon$ of PI in the presence of the pressurized CO_2 to that of neat (bulk) PI in a reference state at $P_{\text{CO}_2} = 0$. We may safely assume that F and g are insensitive to the existence CO_2 ¹¹⁾ and that the total dipole moment per PI chain, p , is constant given that the chain is in the concentrated state where the excluded volume effect is negligible. Then, from eq 1, $b_{p,\varepsilon}$ is expressed in terms of the chain number density ν as

$$b_{p,\varepsilon} = \frac{\nu}{\nu_{\text{ref}}} = \frac{\Delta\varepsilon}{\Delta\varepsilon_{\text{ref}}} \quad (2)$$

Note that this expression of $b_{p,\varepsilon}$ is not affected by the entanglement.¹¹⁾ The $b_{p,\varepsilon}$ data (Figure 4(b)) indicate that the ν/ν_{ref} ratio decreases only to ~ 0.85 with increasing P_{CO_2} up to 10 MPa. Thus, the above assumption of the lack of the excluded volume effect is consistent with the $b_{p,\varepsilon}$ data.

Since the viscoelastic mode distribution of PI260k does not change with P_{CO_2} (cf. Figure 2), the viscoelastic vertical shift factor $b_{p,G}$ of the entangled PI260k is equivalent to a ratio of the plateau modulus G_N in the presence of the pressurized CO_2 to that of neat (bulk) PI in a reference state at $P_{\text{CO}_2} = 0$. Thus, the $b_{p,G}$ factor is affected by the entanglement, as noted from the well known expression of G_N ^{13,18)}

$$G_N = \frac{\nu M}{M_e} k_B T \quad (3)$$

where M is the molecular weight of the chain and the product νM represents the mass concentration, and M_e is the molecular weight between entanglements. M_e in concentrated solutions is related to M_e^0 in bulk and the volume fraction of the polymer ν as

$$M_e = \frac{M_e^0}{\nu^\alpha} \quad (4)$$

where α is the dilation exponent; $\alpha \cong 1.3$ for monodisperse linear PI.¹⁹⁾ Thus, the plateau modulus G_N scales as $\nu^{1+\alpha}$, not ν^1 , which results in the entanglement effect on the viscoelastic $b_{p,G}$ of the well entangled PI260k ($b_{p,G} = G_N/G_N^0 = \nu^{1+\alpha}$). The difference between the dielectric $b_{p,\varepsilon}$ ($= \nu/\nu_{\text{ref}}$) and the viscoelastic $b_{p,G}$ quite possibly reflects this entanglement

Fig. 4. CO_2 pressure dependence of (a) viscoelastic/dielectric horizontal shift factors, $a_{p,G}$ (filled square) and $a_{p,\varepsilon}$ (open triangle), and (b) viscoelastic/dielectric vertical shift factors, $b_{p,G}$ (filled square) and $b_{p,\varepsilon}$ (filled triangle), obtained for PI260k equilibrated under various P_{CO_2} at 25 °C. The unfilled square in panel (b) indicates plots of $b_{p,G}^{1/2.3}$. For further details, see text.

effect. In fact, the volume change on mixing PI and CO₂ can be safely neglected and v is well approximated as v/v_{ref} , which suggests a simple relationship, $b_{p,e} = b_{p,G}^{1/(1+\alpha)}$ with $\alpha \cong 1.3$. This relationship holds within experimental uncertainty (compare the plots of $b_{p,e}$ and $b_{p,G}^{1/2.3}$ in Figure 4(b)), confirming the basic validity of our argument.

4.2 Relationship Between Dielectric and Viscoelastic Relaxation Functions

The global dynamics of entangled linear PI chain is well described by dynamic tube dilation (DTD) mechanism within the framework of the current tube model.^{13,17,19} For monodisperse, entangled linear PI in bulk, the terminal relaxation has been found to be well described by the full-DTD picture that is intimately related to the double reptation picture.^{13,17,19} In the full-DTD picture, the relaxed portions of the chains are regarded as a simple solvent having no contribution to the entanglement, and the normalized viscoelastic and dielectric relaxation functions, $\mu(t)$ ($= G(t)/G_N$) and $\Phi(t)$, are related to the survival fraction of the dilating tube $\varphi'(t)$ as¹⁹

$$\mu(t) = \{\varphi'(t)\}^{1+\alpha} \quad \text{with } \alpha = 1.3 \text{ for PI} \quad (5a)$$

$$\Phi(t) = \varphi'(t) + \text{tube edge fluctuation term} \quad (5b)$$

The “tube edge fluctuation term” in eq 5b indicates the dielectric memory decay due to lateral fluctuation of the chain within the dilating tube. Equations 5a and 5b specify the full-DTD relationship between the viscoelastic $\mu(t)$ and $\Phi(t)$ data that has been confirmed experimentally.¹⁹ This relationship is numerically very close to a simple power-law relationship,¹⁹

$$\mu(t) = \{\Phi(t)\}^2 \quad (6)$$

Thus, we can test the validity of eq 6 for our PI/CO₂ system to examine if the PI/CO₂ system behave as the ordinary solution thereby allowing the mode of global motion of PI therein to remain unaffected by CO₂ and coincide with that of bulk PI.

A comment needs to be made for this test. Differing from the monodisperse PI utilized in the previous test,^{13,17,19} our PI has a rather broad, unimodal molecular weight distribution ($M_w/M_n = 1.7$). However, this unimodal distribution enhances the validity of the molecular picture of full-DTD (and double reptation).²⁰ Thus, the test of eq 6 unequivocally allows us to examine if the PI/CO₂ system behave as the ordinary solution.

For the test of eq 6, we can express the normalized dielectric relaxation function $\Phi(t)$ as a sum of dielectric relaxation modes,

$$\Phi(t) = \sum_p g_p \exp\left(-\frac{t}{\tau_p}\right) \quad \text{with } \sum_p g_p = 1 \quad (7)$$

where τ_p and g_p represent the relaxation time and normalized intensity of p -th mode. The corresponding expression of the data for the decrease of dielectric constant, $\varepsilon_0 - \varepsilon'(\omega)$, and dielectric loss, $\varepsilon''(\omega)$, is given by¹⁷

$$\frac{\varepsilon_0 - \varepsilon'(\omega)}{\Delta\varepsilon} = \sum_p g_p \frac{\omega^2 \tau_p^2}{1 + \omega^2 \tau_p^2}, \quad \frac{\varepsilon''(\omega)}{\Delta\varepsilon} = \sum_p g_p \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2} \quad (8)$$

where $\Delta\varepsilon$ is the dielectric intensity. Applying a previously introduced iterative fitting method²¹ to the $\varepsilon_0 - \varepsilon'(\omega)$ and $\varepsilon''(\omega)$ data, we evaluated τ_p and g_p appearing in eq 8. The solid curves in Figure 2(c) shows $\varepsilon_0 - \varepsilon'(\omega)$ and $\varepsilon''(\omega)$ re-calculated from these τ_p and g_p . Excellent agreement between the curves and the data indicates satisfactory accuracy of the τ_p and g_p obtained from the iterative fitting.

If eq 6 for the full-DTD picture is valid, the complex shear modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$ should be expressed in terms of the dielectric τ_p and g_p determined as above:

$$\frac{G'(\omega) + iG''(\omega)}{G_N} = \sum_{p,q} h_{pq} \frac{\omega^2 \tau_{pq}^2 + i\omega \tau_{pq}}{1 + \omega^2 \tau_{pq}^2} \quad (9a)$$

$$h_{pq} = g_p g_q, \quad \tau_{pq} = [\tau_p^{-1} + \tau_q^{-1}]^{-1} \quad (9b)$$

The $G'(\omega)$ and $G''(\omega)$ calculated from eq 9 are shown in Fig. 3(c) with the dashed and solid curves. These calculated curves excellently agree with the $G'(\omega)$ and $G''(\omega)$ data, indicating that full-DTD relationship holds for PI/CO₂ systems. This result allows us to conclude that the PI260k/CO₂ system is nothing different from linear PI solutions in ordinary solvents (that obey the full-DTD picture) as long as CO₂ pressure is not extremely high (to give a densification effect). Thus, conventional knowledge for ordinary polymer solutions would work for polymer processing with the aid of pressurized CO₂.

5. CONCLUSION

We have conducted viscoelastic and dielectric measurements for entangled linear PI equilibrated under various CO₂ pressures. CO₂ dissolved into PI with increasing CO₂ pressure to accelerate the global motion of PI observed as the viscoelastic and dielectric relaxation. The time - CO₂ pressure superposition worked for the viscoelastic and dielectric data, and the shift factors for the two set of data were consistent to

each other. The dynamic tube dilation relationship between the dielectric and viscoelastic data, being valid for ordinary solutions/bulk of entangled linear PI, was found to hold for the PI/CO₂ system. This result suggests that CO₂ behaves as an ordinary solvent/plasticizer for PI and has no special effect on global dynamics of PI chain.

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