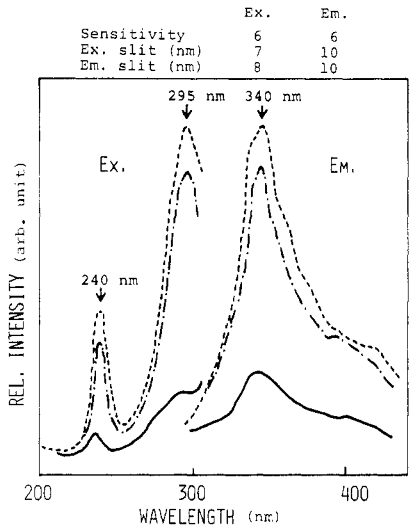

Figure 1. Fluorescence spectra of high-density polyethylene film (- - -), isotactic polypropylene film (–•–), and poly(vinyl chloride) film (—). Uncorrected spectra.

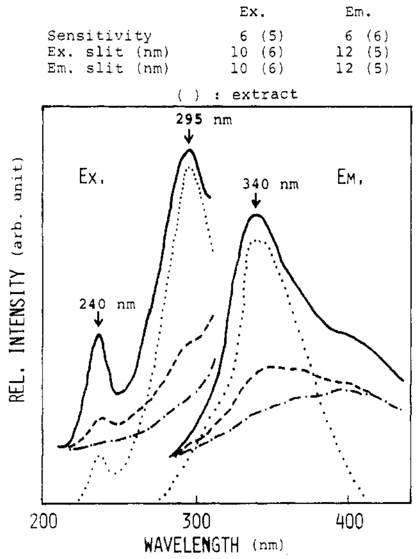

Figure 2. Fluorescence spectra of poly(vinyl chloride): (—) film prepared from an unextracted sample; (–••–) film prepared from an extracted sample after standing for 2 months in an ambient atmosphere; (•••) the extract (hexane solution). Uncorrected spectra.

addition, a broad shoulder observed in the 400-nm region in the unextracted film remains after extraction, but no excitation spectrum corresponding to the 400-nm emission was observed. Therefore, assignment of the shoulder is impossible at present. The results apparently indicate that fluorescence species were extracted from the powdery PVC by hexane and transferred to the hexane.

When a PVC film prepared from the extracted sample showing no fluorescence emission was exposed to the atmosphere for 2 months, a fluorescence spectrum similar to that of the unextracted PVC appeared again. However, the intensity of the spectrum was very weak compared to that of the unextracted film. In the case of HDPE and IPP, the recovery of the intensity of the fluorescence spectra of the extracted film was much faster, reaching that of the unextracted sample after standing ca. 5 h in an ambient atmosphere.[8,9] The differences observed between PVC and polyolefins can probably be ascribed to different affinities of the chromophoric impurities for these polymer.

As mentioned above, the amount of adsorbed chromophoric impurities in PVC was extremely small, but they could be extracted by hexane. In addition, exposure of the extracted PVC film to the atmosphere very slowly formed a fluorescence emission similar to that of unextracted film. Therefore, one can conclude that the fluorescent species in PVC, like those in the polyolefins, are PNA impurities absorbed in the polymer.

Registry No. Poly(vinyl chloride) (homopolymer), 9002-86-2.

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Influence of Entanglement on the Dielectric Normal Mode Process of *cis*-Polyisoprene

Linear flexible polymers having dipoles aligned in the direction parallel to the chain backbone exhibit a dielectric relaxation due to fluctuation of the end-to-end distance.[1-3] In dilute solutions of such a polymer, the dielectric relaxation was described by the Rouse–Zimm theory.[4,5] Thus such a relaxation is referred to as "normal mode process". Experimental studies on the normal mode process are relatively rare.[6-11] Among these, Stockmayer and his coworkers studied this subject most extensively.[6-8] Recently, we also reported the dielectric normal mode process in dilute solutions of poly(2,6-dichloro-1,4-phenylene oxide) and found that the dielectric behavior is virtually in accord with the prediction by the Rouse–Zimm theory.[9] However, the data of the normal model process reported to date are concerned mostly with dilute solutions and not at all with the systems in which polymer chains are entangled with one another. It may be expected easily that entanglements cause an increase in the relaxation time as in the case of viscoelastic relaxation time, which has been explained by the tube theory of de Gennes[12] and of Doi and Edwards.[13] In an effort to explore the influence of entanglement on the dielectric normal mode process, we studied dielectric relaxation in undiluted *cis*-polyisoprene (*cis*-PI). In this communication, we report some preliminary results of the study.

Because of the lack of symmetry in the chemical structure of *cis*-PI, this polymer should have nonzero components of dipole moment both parallel and perpendicular to the chain contour. The perpendicular dipole

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Table I
Weight-Average Molecular Weight M_w, Ratio of Weight- and Number-Average Molecular Weight M_w/M_n, and the Contents (in Percent) of the Cis-1,4, Trans-1,4, and Vinyl-3,4 Linkages

code	$10^4 M_w$	M_w/M_n	cis-1,4	trans-1,4	vinyl-3,4
PI-11	1.10	1.17	83.4	13.0	3.7
PI-16	1.62	1.23	74.3	21.3	4.4
PI-20	2.34	1.20	71.9	22.4	5.6
PI-40	4.19	1.34	83.9	12.3	3.8
PI-60	5.89	1.33	79.4	18.0	2.6
PI-128	12.8	1.37	81.1	14.3	4.7

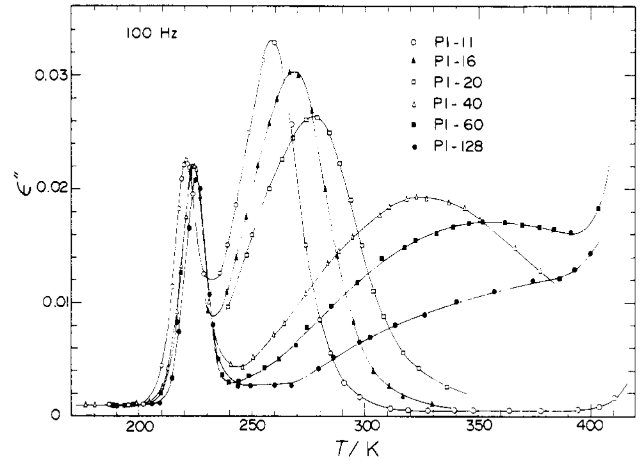

Figure 1. Temperature dependence of ϵ'' at 100 Hz for the undiluted samples of *cis*-polyisoprene with various molecular weights. Sample codes are given in this figure.

causes a dielectric relaxation due to segmental motions as is usually observed for polar amorphous polymers, while the parallel dipole causes the normal mode process.[1,3] At present, however, there are few reports on dielectric relaxations, which are responsible for the parallel dipole moment of *cis*-PI. Bakule and Stoll reported the occurrence of two loss maxima for a bulk natural rubber.[14] They considered that the low-frequency peak originates from either the parallel dipole moment of *cis*-PI or impurities such as protein included in the sample. However, no detailed analysis of the data was given.

Samples of *cis*-polyisoprene were prepared by anionic polymerization in *n*-pentane at room temperature with *n*-butyllithium as the initiator. The polymer samples were stored without addition of any antioxidizing reagents under an atmosphere of helium at about 270 K before use. Weight- and number-average molecular weights (M_w and M_n) were determined by gel permeation chromatography (GPC) by using an instrument equipped with a low-angle light scattering detector. Microstructure of the samples was analyzed by ^{13}C NMR based on the resonance lines due to the methyl carbon atom.[15] The results are summarized in Table I. Dielectric measurements were made over the frequency range 3 Hz to 100 MHz by using transformer bridges (GR 1615A, and Showa Denki) and a twin-T type bridge (Fujisoku DLB 1101D).

Temperature dependences of the dielectric loss factor ϵ'' at 100 Hz are shown in Figure 1. Since the glass transition temperature T_g of *cis*-PI locates at about 195 K, it is obvious that the loss maxima around 220 K are due to the primary relaxation process (α process) and originate from segmental motions of the polymer chain.[16,17] The positions of these loss maxima were almost independent of the molecular weight as is usually observed for amorphous polymers. In contrast to the segmental mode, the loss maxima located above 250 K depended strongly on the molecular weight. They shifted to higher temperature with increasing molecular weight. This behavior is characteristic of normal mode processes and hence these loss maxima can be attributed to a normal mode process.

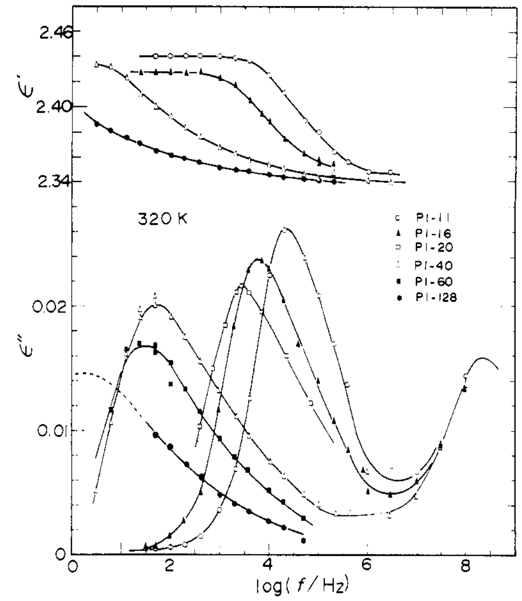

Figure 2. Frequency dependence of ϵ' and ϵ'' at 320 K for the undiluted *cis*-polyisoprene samples.

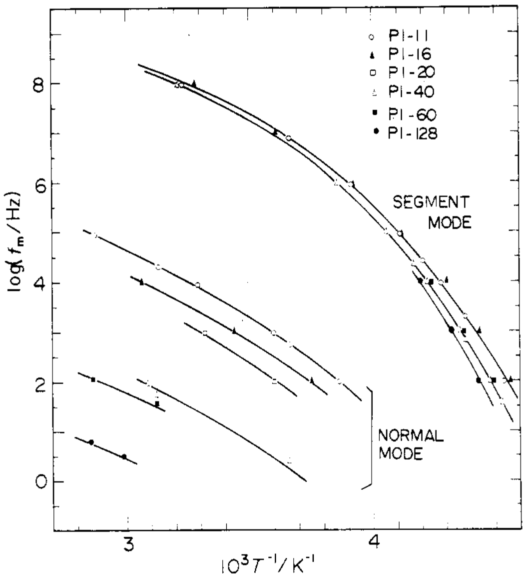

Figure 3. Arrhenius plots for the segmental mode and normal mode for the samples of *cis*-polyisoprene.

Frequency dependences of ϵ' and ϵ'' for the *cis*-PI samples measured at 320 K are shown in Figure 2. Around 100 MHz, the loss maximum due to the segmental mode is seen, while in the frequency region below 100 kHz, loss peaks due to the normal mode process are seen. The frequency dependence curves correspond well to the temperature dependence curves.

The frequencies of the loss maxima for the segmental mode $f_m(s)$ and those for the normal mode $f_m(n)$ are plotted against the inverse of temperature in Figure 3. The logarithm of $f_m(s)$ and that of $f_m(n)$ vary with temperature in an almost parallel manner, indicating that the friction constant $\zeta(s)$ for the segmental motion is approximately proportional to that for the normal mode motion $\zeta(n)$. Strictly speaking, however, we recognize a trend that $f_m(s)/f_m(n)$ tends to decrease slightly with decreasing temperature.

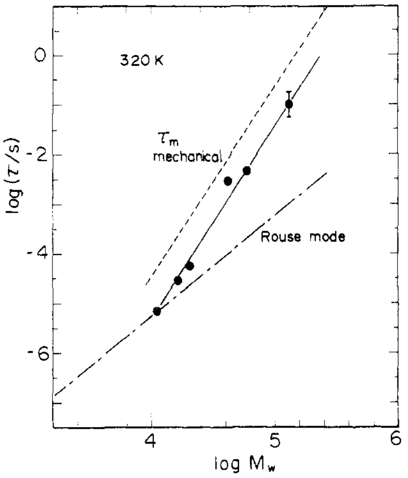

Figure 4. Comparison of the molecular weight dependences of the dielectric relaxation time at 320 K for the normal mode process (●), the mechanical maximum relaxation time reported by Nemoto et al.[18,19] (dashed line), and the dielectric relaxation time predicted by the Rouse theory (eq 1) (dot-dashed line).

The dielectric relaxation time for the normal mode process $\tau_D(n)$ at 320 K given by $\tau_D(n) = 1/(2\pi f_m(n))$ is plotted with respect to the molecular weight M in Figure 4. From the slope of this plot, it is found that $\tau_D(n)$ varies with the 3.7 ± 0.2 power of the molecular weight. This M dependence is stronger than that predicted by the Rouse theory ($\propto M^2$) but is similar to the M dependence of viscoelastic relaxation times in entangled systems, known as the 3.4-power law.

Measurements of shear creep compliance on *cis*-PI samples (84.5% cis) were carried out by Nemoto et al.,[18,19] who reported the maximum viscoelastic relaxation times τ_m at 243 K. For the sake of comparison, the values of τ_m are shifted from 243 to 320 K by using the shift factor reported by the same authors and plotted in Figure 4. Interestingly, τ_D agrees approximately with τ_m and in addition, the molecular weight dependence of τ_D coincides with that of τ_m.

It was also reported by Nemoto et al.[19] that the molecular weight dependence of the viscosity η of *cis*-PI changes at a characteristic molecular weight $M_c = 10\,000 \pm 1000$. The viscosity below M_c is proportional to M, indicating that the chains are not entangled. For undiluted polymers with molecular weight below M_c, the dielectric relaxation time τ_R is given by the Rouse theory[4,5] and is written as[1]

$$\tau_R = 12M\eta/(\pi^2 RT\rho) \qquad (1)$$

where R and ρ denote the gas constant and density, respectively. The M dependence of τ_R calculated with the data of η below M_c is shown in Figure 4, where τ_R is extrapolated to the high molecular weight region for the purpose of comparison. We note that $\tau_D(n)$ for PI-11 having molecular weight close to M_c agrees well with the theoretical relaxation time τ_R. It is expected that if the measurement is made on *cis*-PI with M lower than M_c, the dielectric relaxation time will conform to eq 1 as was found by Baur and Stockmayer for undiluted polypropylene oxide with low molecular weight.[6]

Generally, the 3.4 power law for mechanical relaxation times has been explained by considering the time scale needed for a chain molecule to slip out from entanglement. According to the tube model, this corresponds to the time scale for the tube disengagement process; i.e., a chain molecule moves out of a tube and enters another new tube.[12,13,20] The present data indicate that the dielectric normal mode process of *cis*-PI is closely related to such a molecular motion. Diffusion of the chain (reptation) causes a change in the direction of the end-to-end vector and as a result causes a change in orientational polarization under alternating electric fields.

Further detailed study of the normal mode process is in progress and will be reported in our later publication.

Registry No. *cis*-PI, 9003-31-0.

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