

## Crossover behaviour of dielectric relaxation in isotactic polystyrene: from stretched exponential decay to power law decay

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 5451

(<http://iopscience.iop.org/0953-8984/3/28/020>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 11/05/2010 at 12:22

Please note that [terms and conditions apply](#).

## LETTER TO THE EDITOR

# Crossover behaviour of dielectric relaxation in isotactic polystyrene: from stretched exponential decay to power law decay

Koji Fukao†, Yoshihisa Miyamoto† and Hideki Miyaji‡

† Department of Physics, College of Liberal Arts and Sciences, Kyoto University, Kyoto 606, Japan

‡ Department of Physics, Faculty of Science, Kyoto University, Kyoto 606, Japan

Received 15 May 1991

**Abstract.** Dielectric loss was studied for the  $\alpha$ -relaxation of isotactic polystyrene; the relaxation is associated with the micro-Brownian motion of polymer chains in the amorphous phase. The decay function for the relaxation was calculated directly from the dielectric loss. It was found that the dielectric relaxation becomes slower as the degree of crystallinity increases. It was also found that the relaxation undergoes a crossover from a stretched exponential decay to a power law decay as the relaxation proceeds. Crystallized isotactic polystyrene has a definite crossover time, while amorphous isotactic polystyrene undergoes the crossover through an intermediate region.

Dielectric relaxations of polymeric materials have been widely investigated. In particular, much attention is paid to relaxations in amorphous polymers; the relaxation obeys an empirical equation of stretched exponential decay, termed the Williams–Watts (ww) equation [1]:

$$\varphi(t) = \exp[-(t/\tau)^\beta] \quad (0 < \beta < 1) \quad (1)$$

where  $\tau$  is a relaxation time and  $\beta$  is a constant. This type of decay function is observed not only in dielectric relaxation of polymeric materials but also in the relaxation phenomena of a wide range of disordered systems [2]. Ngai [3] has developed a general phenomenological scheme for treating relaxation processes in disordered systems.

Jonscher [4], on the other hand, proposes another empirical relaxation law for polymeric materials, which is given by

$$-d\varphi/dt \propto [(\omega_p t)^n + (\omega_p t)^{m+1}]^{-1} \quad (0 < n, m < 1) \quad (2)$$

where  $\omega_p$ ,  $m$  and  $n$  are constants. These two empirical formulae have been applied to many polymeric materials. The significant difference between equations (1) and (2) exists in the short and long time ranges; in the intermediate timescale they are similar. Equation (2) leads to a power-law-type decay function in short and long time ranges, while (1) is of a stretched exponential type. Recently, Weron [5] has derived both the stretched exponential decay function and the power law one on the basis of the concept

of fractal time. However, the difference has not yet been discussed sufficiently on the basis of experimental results, because the data fitting is usually made not directly to decay functions, but to the dielectric loss  $\epsilon''(\omega)$  in the frequency range of at most four decades near the loss peak. Furthermore, polymeric materials often exhibit more than two dielectric loss peaks whose tails are overlapping with each other; the frequency range available for the analysis is restricted to the frequency range where each dielectric loss is dominant.

In this letter, we investigate the  $\alpha$ -relaxation (main dispersion) of isotactic polystyrene (IPS), which has been attributed to the micro-Brownian motion of polymer chains in the amorphous phase [6]. We evaluate the decay function directly from the dielectric loss obtained experimentally and compare the decay functions of various samples. The  $\alpha$ -relaxation of IPS is well separated from other relaxations, because the  $\beta$ -relaxation due to the local motion of chains has not been observed in IPS [6, 7]. Further, the growth rate of IPS crystals is so slow [8] that the crystallization condition can easily be controlled. It is therefore possible to evaluate the dependence of decay functions on the fraction of spherulites and the higher-order structure. For example, we can compare the dynamics of polymer chains in the isotropic amorphous phase with that in the 'constrained' amorphous phase intervening between the crystalline layers.

The sample used for dielectric measurement is IPS purchased from Polymer Laboratories Ltd. The weight-averaged molecular weight  $M_w$  is  $5.56 \times 10^5$  and  $M_w/M_n$  is 1.9 ( $M_n$  is the number-averaged molecular weight). Two types of samples were prepared: IPS-A, an amorphous sample (sample (A)) which is quenched to room temperature after melting in vacuo; IPS-X, a crystalline sample (sample (B)) which was isothermally crystallized at 449 K in vacuo and the crystallinity of which is 27%. Gold was evaporated as electrodes onto the samples. The dielectric measurement was made by use of an LCR meter (HP4284A). Sample (A) consists of only isotropic amorphous phase, while sample (B) is filled with spherulites; the  $\alpha$ -relaxation of sample (A) is due to the micro-Brownian motion of polymer chains in the isotropic amorphous phase, while that of sample (B) is due to that in the 'constrained' amorphous phase. In this 'constrained' amorphous phase, there exist loops, cilia emanating from crystals and bridges between them. The dielectric relaxation of this phase, therefore, is expected to be different from that of isotropic amorphous phase.

Figures 1(A) and 1(B) show the frequency dependence of dielectric loss at various temperatures in samples (A) and (B), respectively. Since the glass transition temperature of IPS is about 363 K, the relaxations shown in figure 1 are associated with glass transition and are the  $\alpha$ -relaxations. The relaxation times obey the Vogel-Fulcher-Tammann equation [9], i.e.,  $\tau = \tau_0 \exp(-U/(T - T_0))$ , where  $\tau_0$ ,  $U$  and  $T_0$  are constants. The dielectric strength decreases with increasing crystallinity  $\chi$ . The detailed behaviour of the relaxation times and dielectric strength will be discussed elsewhere [7]. Peak positions and heights are used to normalize the dielectric loss curve. As depicted in figure 2, it is found that the normalized dielectric losses at different temperatures can be reduced to a single master curve. When figures 2(A) and 2(B) are carefully compared with each other, a slight change in the shape of dielectric loss with temperature seems to occur in sample (B). However, this slight deviation is negligible without any significant error in the present analysis. Other crystalline polymers such as polyvinylidene fluoride exhibit much stronger dependence of the shape of the dielectric loss curve on temperature [10].

Comparing the master curve of sample (A) with that of (B), we notice that the amorphous IPS shows an asymmetric loss curve but the crystallized IPS shows a more symmetric one; the loss curve of IPS-X has a shallower slope in the low-frequency side

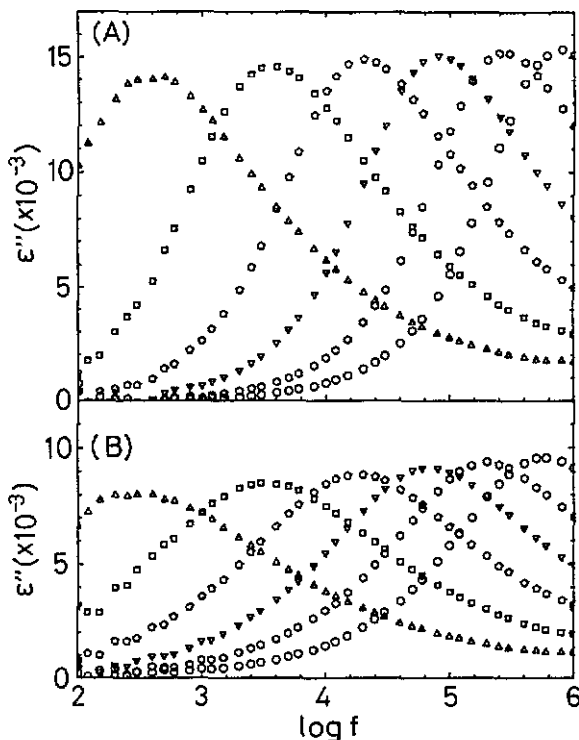


Figure 1. The dependence of dielectric loss of IPS on frequency (Hz) at various temperatures. (A) Amorphous IPS ( $\chi = 0\%$ ) (sample (A)):  $\circ$ , 439.7 K;  $\odot$ , 429.9 K;  $\nabla$ , 420.4 K;  $\diamond$ , 411.0 K;  $\square$ , 401.7 K;  $\triangle$ , 391.4 K;  $\diamond$ , 389.3 K. (B) Crystallized IPS ( $\chi = 27\%$ ) (sample (B)):  $\circ$ , 444.7 K;  $\odot$ , 434.1 K;  $\nabla$ , 424.8 K;  $\diamond$ , 414.9 K;  $\square$ , 404.7 K;  $\triangle$ , 394.2 K;  $\diamond$ , 390.8 K.

than that of IPS-A. In order to discuss the difference in the relaxation behaviours between samples (A) and (B), we calculate the decay function  $\Phi(t)$  from the experimental values of dielectric loss versus frequency according to the relation given by

$$\varphi(t) = \frac{2}{\pi} \int_0^{\infty} \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_{\infty}} \cos \omega t \frac{d\omega}{\omega} \quad (3)$$

where  $\varepsilon_0$  and  $\varepsilon_{\infty}$  are the limiting low- and high-frequency dielectric permittivities, respectively [11]. The calculated  $\varphi(t)$  is given in figures 3 and 4. Overall behaviours of the decay functions in figure 3 are fitted by the ww decay function. The values of  $\beta$  of the ww equation are 0.46 and 0.41 for samples (A) and (B), respectively. This suggests that the increase in crystallinity gives rise to a slower decay function. Further, the relaxation time  $\tau$  is longer for the larger crystallinity [7]. When we carefully compare the fitting curve with the values calculated using equation (3), a slight but systematic deviation from the ww equation is recognized, especially in the long-time region. Figure 4 is a plot of  $\log \Phi$  versus  $\log(t/\tau)$  and clearly shows the existence of the region of a power law decay at long-time tail.

To investigate the change in relaxation behaviour, we adopt the following rate equation:

$$-dN/dt = k(t)N(t) \quad (4)$$

where  $N(t)$  is the number of dipole moments which have not yet relaxed at time  $t$  and  $k(t)$  is a time-dependent rate constant. In this case, since  $\varphi(t) = N(t)/N(0)$ , we can obtain the rate constant in terms of the equation  $k(t) = -\dot{\varphi}(t)/\varphi(t)$ . Figure 5 shows the reduced rate constant  $\tilde{k}(t) (= k(t)\tau$ , where  $\tau$  is independent of time) as a function of

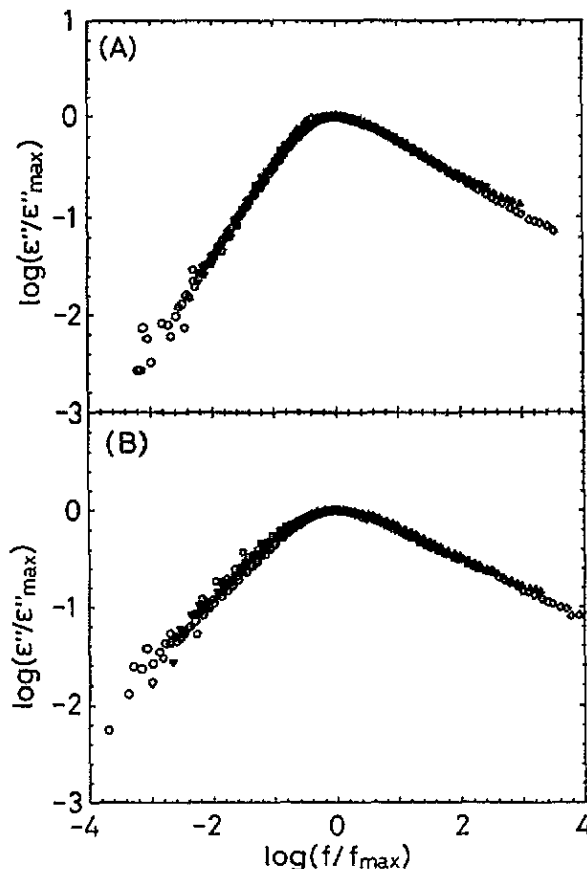


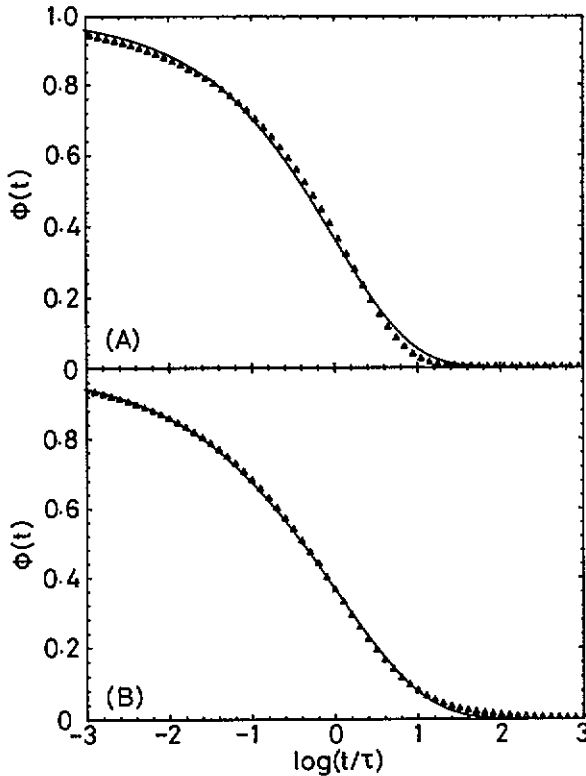
Figure 2. The dependence of reduced dielectric loss ( $\epsilon''/\epsilon''_{\max}$ ) on reduced frequency ( $f/f_{\max}$ ). Here  $f_{\max}$  and  $\epsilon''_{\max}$  are the peak position and the height of the loss curves in figure 1. (A) Amorphous IPS ( $\chi = 0\%$ ) (sample (A)). (B) Crystallized IPS ( $\chi = 27\%$ ) (sample (B)). The symbols are the same as in figure 1.

normalized time  $t/\tau$ . In the case of IPS-X, it is found that  $\hat{k}(t)$  has two different regions where the time dependence of  $k(t)$  are different from each other; that is, one is proportional to  $t^{-0.57}$  (I) and the other is nearly proportional to  $t^{-1}$  (II). These two regions are separated by a definite crossover point at  $t/\tau = 10^{0.6}$  ( $= \hat{t}_B$ ). Here, if  $k(t) \propto t^{\beta-1}$  ( $0 \leq \beta < 1$ ), we can obtain decay functions as follows:

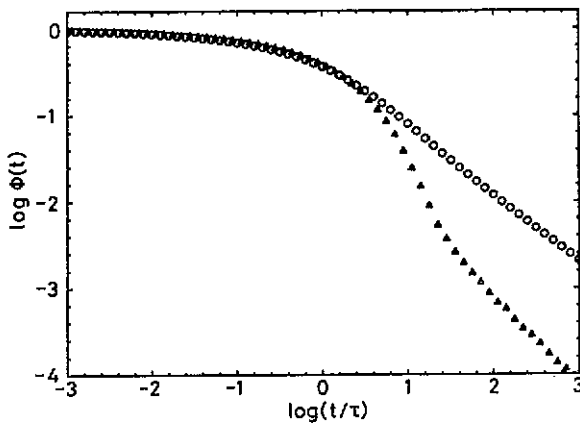
$$\varphi(t) = \begin{cases} \exp[-(t/\tau)^\beta] & (0 < \beta < 1) \\ ct^{-n} & (\beta = 0). \end{cases}$$

Therefore, in IPS-X, the dielectric decay function obeys the ww equation up to  $\hat{t}_B$  and later shows a definite crossover to a power law decay. As shown in figure 5(A), on the other hand, IPS-A has a more complicated dielectric relaxation behaviour. The time dependence of the rate constant can be divided into at least three regions. The first region (I:  $t/\tau < \hat{t}_{A1}$ ) has the same time dependence of rate constant as that of region I in IPS-X and the third region (III:  $t/\tau > \hat{t}_{A2}$ ), region II in IPS-X. The existence of the second region (II:  $\hat{t}_{A1} < t/\tau < \hat{t}_{A2}$ ) leads to the significant difference in  $k(t)$  between IPS-X and IPS-A. Since the time dependence of the rate constant in this region is approximately expressed as  $t^{-0.4}$ , the decay function in this region may be regarded as the ww equation with  $\beta = 0.6$ . The overall relaxation behaviour of IPS-A shown in figure 3 accordingly seems to be a steeper one than that of IPS-X.

In summary, it has been found that the dielectric relaxation behaviour of IPS above the glass transition temperature shows a crossover from a stretched exponential decay



**Figure 3.** The dependence of decay function on reduced time. Full curves are obtained from the ww equation. (A) amorphous IPS ( $\chi = 0\%$ ) (sample (A)),  $\beta = 0.46$ . (B) Crystallized IPS ( $\chi = 27\%$ ) (sample (B)),  $\beta = 0.41$ .



**Figure 4.** The dependence of the logarithm of the decay function on reduced time:  $\Delta$ , amorphous IPS ( $\chi = 0\%$ ) (sample (A));  $\circ$ , crystallized IPS ( $\chi = 27\%$ ) (sample (B)).

to a power law decay. This crossover behaviour depends on the crystallinity of the sample. A crystallized sample has a definite crossover point, while an amorphous sample has an intermediate region between a stretched exponential decay and a power law decay. In this case, equation (2) is valid in the long-time region, while the ww equation is valid in the intermediate-time region or near  $t/\tau = 1$ . It is suggested that neither the empirical equation (1) nor equation (2) is sufficient by itself to reproduce the experimental dielectric loss or decay function of polymeric materials.

One of the authors (KF) thanks the Ministry of Education, Science and Culture of Japan for a Grant-in-Aid.

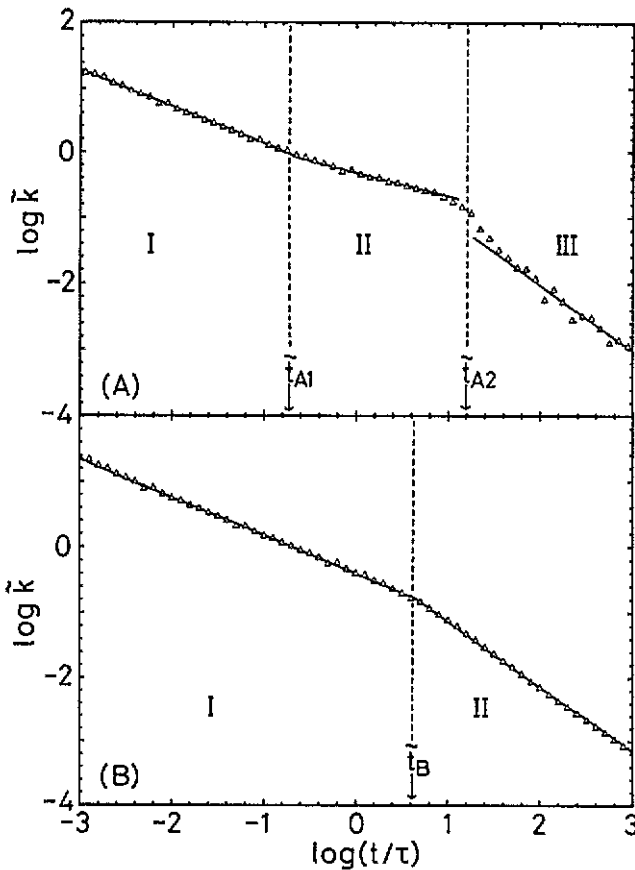


Figure 5. The dependence of the reduced rate constant on reduced time. (A) Amorphous IPS ( $\chi = 0\%$ ) (sample (A)). (B) Crystallized IPS ( $\chi = 27\%$ ) (sample (B)).

## References

- [1] Williams G and Watts D C 1970 *Trans. Faraday Soc.* **66** 80
- [2] Ngai K L 1987 *Non-Debye Relaxation in Condensed Matter* ed T V Ramakrishnan *et al* (Singapore: World Scientific) p 23
- [3] Ngai K L 1979 *Comment. Solid State Phys.* **9** 127
- [4] Jonscher A K 1975 *Colloid Polym. Sci.* **253** 1231; 1975 *Nature* **256** 566
- [5] Weron K 1991 *J. Phys.: Condens. Matter* **3** 221
- [6] Yano O and Wada Y 1971 *J. Polym. Sci.* **A2** **9** 669
- [7] Fukao K, Miyamoto Y and Miyaji H 1991 in preparation
- [8] Suzuki T and Kovacs A J 1970 *Polym. J.* **1** 82
- [9] Vogel H 1921 *Z. Phys* **22** 645  
Fulcher G 1925 *J. Am. Ceram. Soc.* **8** 339  
Tammann G and Hesse N 1926 *Z. Anorg. Chem.* **156** 245
- [10] Sasabe H, Saito S, Asahina M and Kakutani H 1969 *J. Polym. Sci.* **A2** **7** 1405
- [11] Cook M, Watts D C and Williams G 1970 *Trans. Faraday Soc.* **66** 2503