Wissenschaftliche Kurzberichte

Kurz-Mitteilungen sichern rasch die Priorität. Die Verantwortung für den Inhalt trägt der Autor. Erscheinungstermin ca. innerhalb 2–6 Wochen nach Einreichung. Umfang der deutlich (Formeln!) geschriebenen Manuskripte bis zu 2 Maschinenseiten. Abbildungen vermeiden. Sonst klischierfähige Zeichnungen mit Beschriftung in weichem Blei. Sonderdruckfreizemplare wie bei Originalarbeiten. Manuskripte an: Prof. F. H. Müller, Marburg/L., Georg-Voigt-Str. 5.

Herausgeber und Verlag

From Department of Electronics and Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka (Japan)

Note on the Lemniscate Law for the Dielectric α -Absorption in Some Amorphous High Polymers

By Kaoru Yamafuji*), Hayao Ichikawa*), Fujio Irie*) and Yōichi Ishida**)

With 1 figure

(Received January 3, 1962)

Davidson and Cole (1) pointed out that the formula for the complex dielectric constant $\epsilon^*(i\omega)$,

$$[\epsilon^*(i\omega) - \epsilon_\infty]/[\epsilon_0 - \epsilon_\infty] = 1/[1 + i\omega\tau]^\beta \quad [1]$$

could satisfy the observed data of the dielectric dispersion in some materials such as glycerine. In equation [1], ω is the angular frequency of the external electric field, τ is a parameter for the relaxation time and β is a parameter which can take the value between 0 and 1. The drawing curve of eq. [1] in $\epsilon' - \epsilon''$ plane becomes lemniscate in the special case of $\beta = 1/2$ and hence eq. [1] is so called the lemniscate law. The lemniscate law is, however, only an experimental law and seems to have no foundation from the molecular theory at present.

Fig. 1. Comparison of the observed data with the lemniscate law ($\beta = 1/2$) and the theoretical curve calculated by eq. [2]

In solid linear high polymers, two sorts of the dielectric dispersions coming from their amorphous parts are in general observed for each sample. We shall call the higher temperature dispersion the α -absorption and the lower temperature one the β -absorption. Although the shape of these dielectric absorption seems to be rather symmetric (2), their shapes are not completely symmetric in $\epsilon'' - \log f$ plane (3). For instance, the dielectric α -absorption in polyvinyl acetate measured by Mead and Fuoss (4) seems to satisfy the Davidson-Cole's law rather than the Cole-Cole's circular arc law. In fig. 1, the observed data (3) for the dielectric α -absorption in polyvinyl acetate are compared with the lemniscate ($\beta = 1/2$). The observed data (3) seem to satisfy the Davidson-Cole's curve ($\beta \simeq 1/2$) at the temperatures much higher than T_g .

On the other hand, the equation in which the inter-chain interactions are added to the usual Rouse-

Zimm (5) equation leads to the following results (6) for the dielectric α -absorption of the completely amorphous polymer at the temperatures far above T_g :

$$[\epsilon^*(i\omega) - \epsilon_\infty]/[\epsilon_0 - \epsilon_\infty] = 1/[(1 + i\omega\tau_0 x)(1 + i\omega\tau_0 x^{-1})]^{1/2} \quad [2]$$

where x is approximately given by

$$x \simeq [(4A + B + C)/(B + C)]^{1/2} \quad [3]$$

In equation [3], A is the restoring force constant between the neighboring segments along the main chain, B is the restoring force constant between the neighboring segments among the neighboring chains and C is the term due to the dipole-dipole interactions, and hence x would take the value between 5 and 30 in usual amorphous linear high polymer (3). Equation [2] approaches to the Debye formula,

$$[\epsilon^*(i\omega) - \epsilon_\infty]/[\epsilon_0 - \epsilon_\infty] = 1/[1 + i\omega\tau]$$

in the limit of $x \rightarrow 1$ (i. e. in the case of $A \ll B + C$).

In usual case of the amorphous high polymer, however, x is far larger than unity (3) and hence eq. [2] approaches to the lemniscate curve ($\beta = 1/2$) in the frequency range $\omega \ll (\tau_0 x^{-1})^{-1}$. In fig. 1, the curves of eq. [2] are compared with the lemniscate ($\beta = 1/2$). As x becomes larger, eq. [2] rapidly approaches to the lemniscate curve ($\beta = 1/2$).

Since the Rouse-Zimm equation [5] as well as its extended one (6) neglect the interactions inside each segment, eq. [2] could not be so good approximation in the very higher frequency range (i. e. in the tail of the higher frequency side of the absorption curve). The more detailed theory in which such interactions are taken into account would, therefore, be expected to approach to the lemniscate law and the foundation of the lemniscate law could be given from the molecular theory at least for the case of the dielectric α -absorption in the amorphous high polymer, although the theoretical equation may or may not be in accordance with eq. [1].

References

- 1) Davidson, D. W. and R. H. Cole, J. Chem. Phys. **18**, 1417 (1950); **19**, 1487 (1951).
- 2) Yamafuji, K. and Y. Ishida, Kolloid-Z. **175**, 27 (1961).
- 3) Ishida, Y., M. Matsuo and K. Yamafuji, *ibid.* (in press).
- 4) Mead, D. J. and R. M. Fuoss, J. Amer. Chem. Soc. **63**, 2832 (1941).
- 5) Rouse, R. E. Jr., J. Chem. Phys. **21**, 1272 (1953); Zimm, B. H., J. Chem. Phys. **24**, 269 (1956).
- 6) Yamafuji, K. and Y. Ishida, Kolloid-Z. (in press)

*) Dept. of Electronics.

**) Dept. of Applied Chemistry.