

Monte Carlo Study on Dielectric Loss Curve for Polymers with Perpendicular—Dipoles

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(Received March 28, 1977)

ABSTRACT: The asymmetry of the dielectric loss curve observed in vinyl-type polymer solutions is investigated by means of the Monte Carlo method. The loss curve is calculated from the Fourier transformation of the decay function which is obtained by using the Monte Carlo method. The model used for a polymer chain in this paper is a chain composed of connected beads lying on the cubic lattice. The following three cases are discussed: Case 1 concerns the random coil chain; symmetric loss curve is obtained. Case 2 has to do with the non-self-intersecting model; the asymmetric loss curve is obtained, but it differs from that derived through experiments in that the experimental curve is more asymmetric, broader on the high frequency side. In Case 3, random numbers are used, taking the correlation into account. In this case the loss curve obtained is asymmetric and is in fairly good agreement with the experimental curve. The results suggest that the most important factor for the appearance of the asymmetric loss curve of vinyl-type polymer in dilute solutions is the correlated molecular motion of the motional units.

KEY WORDS Monte Carlo Method / Random Number / Asymmetry / Correlated Molecular Motion / Dielectric Loss Curve / Vinyl-Type Polymer / Dipoles /

Dielectric measurements on dilute solutions of polar polymers offer important information on chain motion. In particular vinyl-type polymers having dipoles attached rigidly and perpendicularly to the chain backbone give important information, since the change in the direction of the dipoles requires a change in the conformation of the chain backbone. It has been reported¹ that the dielectric loss curves (ϵ'' vs. $\log(f)$) of vinyl-type polymers are asymmetric, being broader on the high frequency side, and independent of the molecular weight, temperature, and solvent. The experimental data suggest that the asymmetry of the loss curve is the characteristic feature in vinyl-type polymers. A number of theories²⁻⁷ have been proposed to interpret the shape of the loss curve, but none of them seems to explain the experimental results in a satisfactory manner. Recently Shore

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and Zwanzig reported⁸ a model which consists of a one-dimensional lattice of objects called spins which are free to rotate in a plane perpendicular to the common axis. The results they obtained indicated that an asymmetric loss curve is observed when the dipolar relaxation, reflecting a correlated molecular motion, occurs in a viscous medium owing to an appropriate strength of interactions between moving units in the chain. These results are very interesting and seem to be consistent with many experimental data. However there is a difference between the model suggested by them and the real chain, because their model is a one dimensional Ising-like model while a real chain motion is a three dimensional one.

The purpose of this paper is to investigate the asymmetric loss curve of vinyl-type polymer in a dilute solution by the Monte Carlo method. Molecular motions of dipolar units are simulated by the change of the position of the beads.

The application of the Monte Carlo method to the investigation of polymers was given for the first time by Verdier and co-workers⁹⁻¹¹ in terms of the behaviour of the square of end-to-end distances with and without excluded volume restrictions. Various problems^{12,13} in polymer physics have been studied by means of the Monte Carlo method but to our knowledge no application of the Monte Carlo method has been made to the problem of the dielectric relaxation spectrum of polymers.

Remarkable results obtained indicate that the existence of a correlated molecular motion of the motional unit is one of the most important factors for the appearance of the asymmetry in the loss curve.

It is shown that the decay function is obtained by eq 6 in the case of the Monte Carlo method. Consequently the loss curve (ϵ'' vs. $\log(f)$) can be calculated. The procedure of the simulation of the micro-Brownian motion is shown and the three cases are discussed.

METHOD OF CALCULATION

The dielectric response of materials is summarized in terms of dielectric constant $\epsilon'(\omega)$ and the loss factor $\epsilon''(\omega)$ by the complex dielectric constant $\epsilon^*(i\omega) = \epsilon' - i\epsilon''$. $\epsilon^*(i\omega)$ is given by the following macroscopic relation:¹⁴

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty -\frac{d\Phi(t)}{dt} \exp(-i\omega t) dt \quad (1)$$

ϵ_0 and ϵ_∞ are the limiting low- and high-frequency dielectric constants, respectively. $\Phi(t)$ is the normalized decay function of the polarization when a steady macroscopic electric field is removed from the materials. Equation 1 shows that the normalized complex dielectric constant is given by the one-sided Fourier transformation of the quantity $-d\Phi/dt$. It follows from eq 1 that

$$\frac{\epsilon'(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty -\frac{d\Phi(t)}{dt} \cos(\omega t) dt \quad (2)$$

$$\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty -\frac{d\Phi(t)}{dt} \sin(\omega t) dt \quad (3)$$

If the decay function $\Phi(t)$ can be calculated on a certain model, the dielectric loss curve (ϵ'' vs. $\log(f)$) is given in terms of eq 3. Dipole decay function is written as follows.

$$\Phi(t) = \frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle}{\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle} \quad (4)$$

where $\mathbf{M}(0)$ and $\mathbf{M}(t)$ is the dipole moment of a chain at the times 0 and t respectively. \mathbf{M} is the vector sum of the elementary dipoles μ_i of the polymer chain. The angle brackets denote the average over the possible conformations of the chain in equilibrium. In that the ergodic hypothesis may be possible for a sufficiently long time interval T , the average $\langle \dots \rangle$ of eq 4 can be replaced as follows.

$$\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle = \frac{1}{T} \int_0^T \mathbf{M}(t') \cdot \mathbf{M}(t+t') dt' \quad (5)$$

In our case the total dipole moment $\mathbf{M}(t)$ is calculated and recorded at each step which is repeated by means of the Monte Carlo method. Therefore eq 5 is reduced to

$$\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle = \frac{1}{N_s - t + 1} \sum_{j=0}^{N_s-t} \mathbf{M}(j) \cdot \mathbf{M}(t+j) \quad (6)$$

where N_s is the number of repeated steps of the random process. Our choice of the number of repeated steps is based on the following consideration. The value of $\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle$ calculated by eq 6 should be independent of initial conformation of the chain. One may expect quite naturally that the large number of N_s removes the effect of the initial conformations. According to Lowry¹⁵ the statistical error represents the order of $(N_s/\tau)^{-1/2}$, where τ is the time in which the effect of the initial conformations vanishes. In order to keep this error within 5%, the number of N_s should be chosen as $N_s = 400\tau$. In this paper N_s is chosen as 40,000.

The dipole decay function $\Phi(t)$ can be obtained by eq 4 and 6, as follows.

$$\Phi(t) = \frac{N_s + 1}{N_s - t + 1} \cdot \frac{\sum_{j=0}^{N_s-t} \mathbf{M}(j) \cdot \mathbf{M}(t+j)}{\sum_{j=0}^{N_s} \mathbf{M}(j) \cdot \mathbf{M}(j)} \quad (7)$$

Following all this, the loss curve (ϵ'' vs. $\log(f)$) can be obtained. It follows from eq 3 that

$$\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty -\frac{d}{dt} \left[\frac{N_s + 1}{N_s - t + 1} \cdot \frac{\sum_{j=0}^{N_s-t} \mathbf{M}(j) \cdot \mathbf{M}(t+j)}{\sum_{j=0}^{N_s} \mathbf{M}(j) \cdot \mathbf{M}(j)} \right] \times \sin(\omega t) dt \quad (8)$$

PROCEDURE FOR SIMULATION

The model for a polymer chain used in this paper is a chain of connected beads lying on the lattice points of a cubic lattice, with the connections between adjacent beads lying along cube edges. The micro-Brownian motion of the polymers in dilute solution is simulated by the Monte Carlo method, using this cubic lattice model as following procedure.

First, the initial conformation of the chain is determined by the random numbers. In this case, the random numbers one to six are generated, corresponding to the unit vectors of the cubic lattice as illustrated in Figure 1. As the selection of the position for the first bead may be arbitrary, we made it the origin. The position for the second bead is determined by a random number chosen within the range from one to six, and the position of the third bead

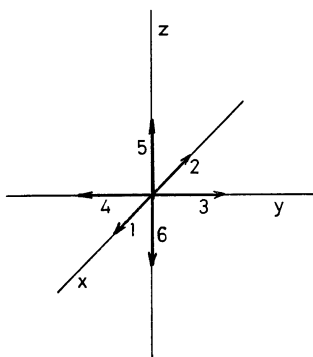


Figure 1. Direction of the unit vectors: the random numbers from one to six correspond to the directions of the unit vectors illustrated by arrows.

is determined by another random number within this range. This procedure is repeated N th times where N is the total number of beads.

Vinyl-type polymers have the dipoles attached rigidly and perpendicular to the chain backbone. The arrangement of dipoles is determined by these random numbers. In this case the random numbers one to four are generated and correspond to the directions perpendicular to the bond of the chain as illustrated in Figure 2. This procedure for the determination of the dipole arrangement is performed for each bond. In Figure 3, one example of initial conformation is shown.

Next, we assume that the micro-Brownian motion of the chain can be simulated by the transition of the position of the randomly selected bead, and by the reorientation of the dipoles. The transition of the position of the bead is assumed to obey the following rule: if the n th bead is selected, the position of n th bead R_n is changed to a new position R_n' as shown by the following:

$$R_n' = R_{n-1} + R_{n+1} - R_n \quad (2 \leq n \leq N-1)$$

$$R_n' = R_n + a \quad \text{or} \quad R_n' = R_n - a \quad (n=1, N)$$

where a is the unit vector of the lattice.

For example if the bond $R_{n+1} - R_n$ is perpendicular to the bond $R_n - R_{n-1}$, the n th bead jumps to the diagonally opposite corner of the square determined by these bonds in three dimensional space. The orientation of the dipole altered along with the transition of the backbone chain, is determined by the random numbers one to four. These random numbers are

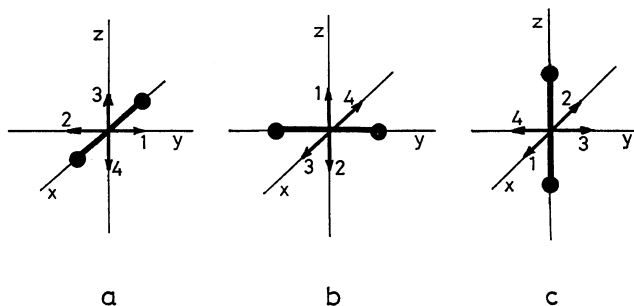


Figure 2. Directions of dipoles: the random numbers one to four correspond to the directions perpendicular to the backbone chain illustrated by arrows: (a) the bond is parallel to x -axis; (b) the bond is parallel to y -axis; (c) the bond is parallel to z -axis.

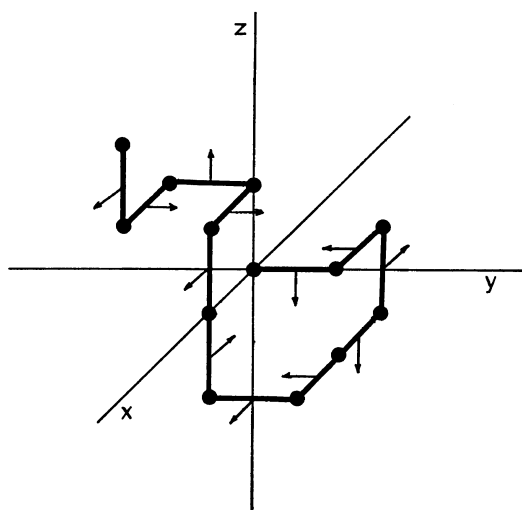


Figure 3. Initial conformation of chain: the bond vectors are determined successively by the random numbers, 3, 2, 6, 1, ...; the directions of the dipoles are determined successively by the random numbers, 2, 2, 2, 4, ...

generated each time the transition of the backbone chain occurs. For example, as illustrated in Figure 4, when the 6th bead is selected, the bead jumps to a new position according to the above, and successively the orientation of the two dipoles which attach to the 5th bond and the 6th bond are altered by the random numbers 4 and 4, respectively. This procedure is repeated 40,000 times as stated above.

These three cases, in terms of the transition of the position of the bead, are treated in this paper. In all cases the number of the beads in chain is chosen as 50. In Case 1 the bonds of the chain are allowed to intersect with themselves, so that Case 1 corresponds to the random coil chain. In Case 2 no bonds are allowed to intersect with themselves, so this case corresponds to a chain with excluded volume, and we denote this case as a non-self-intersecting one. In Case 1 and Case 2, the probability of selection of the bead number for the transition is equivalent to that among all beads. On the other hand, in Case 3, the random numbers which have the Gaussian distribution are generated for the successive selection of the bead number, so the probability of selecting the bead for the transition is not uniform in the chain.

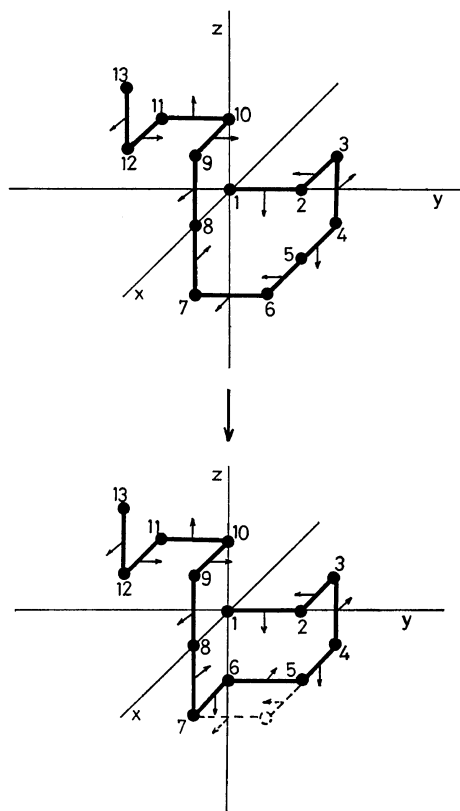


Figure 4. Change of the conformation of the chain.

For example if the 6th bead is selected initially, the probability of selecting the 5th bead or the 7th bead near the 6th bead is larger than the probability that the 13th bead far from the 6th bead will be selected for the successive events. Consequently if the 8th bead is selected, the probability of selecting the bead near the 8th bead is larger. Differing from Case 1 and Case 2, in Case 3 some correlation of the behavior of the transition of the bead is taken into consideration. The magnitude of the correlation depends on the dispersion constant σ of the Gaussian distribution. In Case 3 both instances of the random coil chain and of the non-self-intersecting are treated.

RESULTS AND DISCUSSION

The dielectric loss curve obtained in Case 1 is symmetric. Only the effect of connectivity

of polymer chain is taken into consideration since this case corresponds to the simulation of random coil chains. The result in Case 1 is quite different from that of the two dimensional case.¹⁶ In the two dimensional case the asymmetric loss curve is obtained both in the random coil case and in the non-self-intersecting case. This result implies that only if a polymer has the dipoles attached rigidly and perpendicular to the chain backbone, is the asymmetric loss curve in all cases obtained. But the result in Case 1 in terms of the three dimensional Monte Carlo method suggests that the asymmetry of the curve of vinyl-type polymer is not subject only to the arrangement of its dipoles. The loss curve obtained in Case 2 is asymmetric to a small extent but this is not in agreement with the experimental loss curve of vinyl-type polymer in dilute solutions; the experimental curve is more asymmetric, and broader on the high frequency side. This shows that the effect of the excluded volume contributes to the asymmetry of the loss curve, but that the asymmetry of the experimental curve cannot be interpreted only by the effect of excluded volume. In the

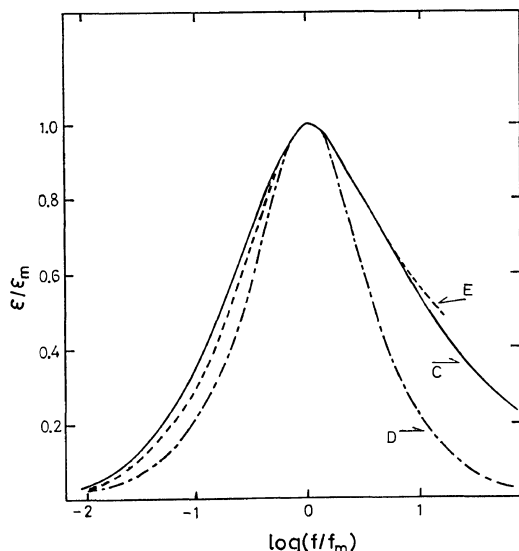


Figure 5. Dielectric loss curve: (C) is the calculated loss curve obtained on non-self-intersecting with $\sigma=N/3$ in Case 3; (D) is the Debye's case in which the loss curve is symmetric; (E) is the experimental loss curve of vinyl-type polymer in dilute solution.

two dimensional case the effect of excluded volume shows a negative contribution to the asymmetry. Hilhorst and Deutch have reported¹⁷ recently that the effect of excluded volume on the kinetics of polymer chains in a lattice model imposes certain rigorous constraints on the chain motion. They also reported that the Monte Carlo calculations in the presence of excluded volume are subject to the specific choice of the kinetics rather than to the intrinsic nature of the excluded volume interaction. These constraints on the kinetics are more severe in the two dimensional case than that in the three dimensional case, so that the negative contribution to asymmetry in two dimensional case is not very reasonable. Verdier and co-workers⁹⁻¹¹ have reported that there is a large increase in the relaxation times in the presence of excluded volume restrictions. It has been also reported that the end-to-end distance correlation function which decay exponentially in the absence of excluded volume becomes strongly nonexponential in the presence of excluded volume restrictions. However in our calculation of the dipole-dipole decay function, the two behaviors in terms of excluded volume mentioned above by Verdier are not observed. The results in Case 2 are not subject to the specific choice of the kinetics, so the effect of excluded volume on the kinetics in the lattice model seems to show the reasonable effect in this work. The loss curve obtained in Case 3 is more asymmetric, broader on the high-frequency side than that obtained in Case 2. Particularly, the loss curve obtained in a non-self-intersecting case with the dispersion constant $\sigma=N/3$ of the Gaussian distribution is in fairly good agreement with the experimental curve of vinyl-type polymer in dilute solution as shown in Figure 5. This result suggests that the correlation of the motional unit contributes greatly to the asymmetry of the loss curve.

In this paper we make use of the empirical decay function suggested by Williams¹⁸ in order to investigate the correspondence between the results obtained in the various cases and the function. The empirical decay function is represented as follows.

$$\Phi_e = \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \quad (9)$$

If $\beta=1$, Φ_e is reduced to the Debye's case in which the loss curve is symmetric. It is reported that as the value of β decreases, the loss curve is more asymmetric, broader on the high frequency side. We found that the loss curve calculated from the empirical decay function agrees with the observed loss curve of vinyl-type polymer in dilute solution when β is about 0.55. The dipole decay function obtained in various cases can be represented approximately by the function mentioned above. The values of β which are estimated by the dipole decay functions are listed in Table I. The calculation of β is carried out by the least squares method. As the value for σ becomes smaller, so does the value for β . This tendency is observed commonly both in the random coil case and in the non-self-intersecting case. These results show the loss curve becomes progressively asymmetric with smaller values of σ . The correlation of the motional unit associated with the dispersion constant σ seems to be the cause of the asymmetry in loss curve. Unfortunately it is difficult to discuss the exact relation between the correlation of chain motion and the value of σ at this stage. Therefore we cannot at the present stage show exactly the kind of chain motion correlation contributing to the asymmetry.

In Table I τ is the relaxation time for the dipole decay function. It should be noted that it is meaningless to discuss the absolute value of relaxation time in this case, because there is no unique relation between the time interval

in the real world and the number of steps in the random process by the Monte Carlo method. Furthermore, the variation of relaxation time shifts the peak of the loss curve parallel to the abscissa and does not depend on the shape of loss curve. However it is interesting to study the relation between the relative variation of relaxation time and the effect of temperature. It may be possible to discuss the effect of temperature by using the Metropolis-Teller method.¹⁹ This problem is under study.

CONCLUSIONS

Even if a polymer has the dipoles rigidly perpendicular to the backbone chain, the dielectric loss curve of the polymer does not always show the asymmetric shape. In other words the asymmetry of the dielectric loss curve is not subject to the arrangement of dipoles, but to the other factors, for example, chain motion. The effect of excluded volume contributes to the asymmetry of the loss curve, but its effect is not the important factor. One of the most important factors for the appearance of the asymmetry of the loss curve is the correlated molecular motion of the motional units, which is simulated in terms of the random numbers with the Gaussian distribution in this paper.

Acknowledgments. The authors wish to express their sincere appreciation to Professor N. Saitô of Waseda University for his illuminating suggestions. Thanks are due also to Dr. Y. Iwasa of Waseda University for his helpful discussions and informations about experiments.

Note added in proof

A very recent paper (F. Géný and L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1 (1977)) shows that the asymmetric loss curve observed for poly(*p*-chlorostyrene) in dilute solution is explainable by using the autocorrelation function of orientations for the polymeric chain derived by Valeur, *et al.*²⁰ We are very stimulated by their work since it is on the basis of the model of conformational jumps in a chain described in a tetrahedral lattice.

Table I. Relaxation time τ , and β calculated from the decay function

Case	σ	τ	β	
Case 1	—	8.0	1.09	*
Case 2	—	9.3	0.92	**
Case 3	N/2	10.4	0.91	
	N/3	19.5	0.54	*
	N/5	147	0.34	
	N/2	11.5	0.76	
	N/3	18.9	0.59	**
	N/5	44.1	0.37	

* Random-coil.

** Non-self-intersecting.

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