Glass Transition in Polymers

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INTRODUCTION

Many authors[1-3] have discussed the nature and origins of the glass transition in polymers, which can be detected by numerous methods. During recent years, the prevalent opinion[1] has been that the transition is an apparent one that it can be interpreted as the temperature point at which the rate of attainment of equilibrium is of the same order of magnitude as the time scale of ordinary physical experiments. This conclusion is based on two experimental facts: the transition as measured by volume expansion shows strong time effects and seems to disappear when equilibrium is attained;[2] the transition determined as the temperature where dynamic mechanical or dielectric loss is maximum shifts with frequency. In many dynamic mechanical or dielectric studies on the transition, only the relaxation effect has been considered. Therefore the above conclusion, on the basis of such experiments, implies that the transition includes time effects, but may not give direct evidence that the transition is not a thermodynamic one.

Dielectric properties of polar materials are described by quantities related to the relaxation mechanism of dipoles and quantities related to molecular structure. According to the Debye theory,[4] complex dielectric constant ϵ^* is represented by following equation:

$$\epsilon^* = \epsilon' - i\epsilon''$$
$$= \epsilon_\infty + [(\epsilon_0 - \epsilon_\infty)/(1 + \omega^2\tau^2)]$$
$$- [i(\epsilon_0 - \epsilon_\infty)\omega\tau/(1 + \omega^2\tau^2)] \quad (1)$$

where ϵ' and ϵ'' are dielectric constant and loss, ω is angular frequency, τ is relaxation time, ϵ_0 is the low-frequency limiting value of the dielectric constant, and ϵ_∞ is the high-frequency limiting value of the dielectric constant. The value of $\epsilon_0 - \epsilon_\infty$ which is independent of frequency and represents the magnitude of dielectric dispersion is given by the following equation:[5]

$$\epsilon_0 - \epsilon_\infty = [3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)][(\epsilon_\infty + 2)/3]^2$$
$$\times (4\pi ng\mu^2/3kT) \quad (2)$$

where n is the concentration of dipoles, μ is the dipole moment, g is a parameter relating to dipole-dipole interactions, k is the Boltzmann constant, and T is the absolute temperature. For several low molecular weight solids, it has been found that the value of $\epsilon_0 - \epsilon_\infty$ changes sharply in some temperature range.[6] The authors have found that for several polymers the value changes in the glass transition range.[7] In the present work, the following problems will be discussed: (1) Is the above-mentioned transition of $\epsilon_0 - \epsilon_\infty$ observed for any polymer? (2) For polymers in which the transition of $\epsilon_0 - \epsilon_\infty$ is observed, does the transition by volume expansion exist when equilibrium is attained? (3) For polymers in which the transition of $\epsilon_0 - \epsilon_\infty$ is not observed, how does the volume change with temperature when equilibrium is attained?

EXPERIMENTAL

Materials

Polymers used in this experiment were polyvinyl acetate (PVAc), polystyrene (PS), polymethyl methacrylate (PMMA), vinylidene chloride–vinyl chloride copolymer (PVDC), polyethylene terephthalate (PET), and polyacrylonitrile (PAN). The test specimens of PVAc, PS, and PMMA were sheets which did not contain plasticizer, filler, or other materials. The specimen of PVDC was a pressed sheet whose composition was VD 80:VC 20:plasticizer 5. The specimen of PET was an amorphous Melinex sheet manufactured by Imperial Chemical Industries, Ltd. The sample of PAN was powder and did not contain other materials.

Apparatus and Procedure

The dielectric measurements were carried out over the frequency range of 0.1 cycles/sec. to 1 Mcycle/sec. and the temperature range of -23 to $+140°C$. The measuring devices used were an inductive-ratio-arm bridge for frequencies above 30 cycles/sec. and a modified resistive-ratio-arm bridge for frequencies below 10 cycles/sec. Both have been described previously.[8] Sheet specimens were coated with a conductive silver paint and baked at a low temperature before being placed between the electrode plates in a measuring cell.[2] The powdered sample was poured into a concentric cylinder electrode system for liquid dielectrics and then the electrode was set in the measuring cell. Though in the case of the powdered sample, observed values of ϵ' or ϵ'' were different from the real values of the sample, the apparent values were useful enough for our purpose.

For some samples, the absorption currents that flowed after the sudden application of d.c. voltage were measured as functions of time over the range of 10 to 1000 sec. The apparatus used was a d.c. amplifier[9] constructed in our laboratory.

Usually, the absorption current is given by the empirical equation $\phi(t) = Kt^{-n}$ where $\phi(t)$ is the absorption current under unit voltage, t is time, and K and n are constants for a particular material at a particular temperature. In the range of $0.3 < n < 1.2$, ϵ'' can be calculated approximately by the following equation:[10]

$$\epsilon'' \simeq [G_0 + \phi(0.1/f)]/2\pi f C_a \qquad (3)$$

where G_0 is steady-state d.c. conductance, f is frequency, and C_a is the capacitance of the electrodes when the sample is replaced by air. The values of ϵ'' over the frequency range of 10^{-2} to 10^{-4} cycles/sec. can thus be obtained from the values of $\phi(t)$ over the range of 10 to 1000 sec. Any value of ϵ'' shown in the following section is that for which the loss component due to steady-state d-c conductance has been subtracted from the total loss. The frequency dependences of ϵ' and ϵ'' at the highest temperature, which is considerably higher than the glass transition temperature T_g, were measured initially, and subsequently those at lower temperatures were measured. The rate of cooling was about $0.1°C./min$.

The volume vs. temperature relationship was measured at a cooling rate of $0.3°C./min$. by means of a dilatometer containing polymer and mercury. Measurements of volume relaxation were carried out by the following procedure. A dilatometer was quickly transferred from a bath at a temperature T_s (about $25°C$. above T_g) to a second constant-temperature bath at a lower temperature T_r. Then the change in volume was observed as a function of time. Subsequently, the polymer was again heated to T_s and the above procedure repeated at a different T_r. A cathetometer was used to determine the height of mercury in the capillary of the dilatometer.

RESULTS AND DISCUSSION

Dielectric Data

For the six polymers, the frequency dependences of ϵ'' at various temperatures are shown in Figures 1–6. The values of ϵ'' at frequencies below 10^{-2} cycles/sec. were obtained by the d-c measurements. Though in reality, two or three dielectric absorptions can be observed for each individual polymer, only the absorption closely related to the glass transition is shown here. The absorptions located in the higher frequency region (Figs. 3 and 5) are not considered in the present study, since they are due to molecular motions, such as the motion of side chains, having little connection with the glass transition.

Temperature dependences of the positions and the magnitudes of the dielectric absorptions are shown in Figure 7. f_{max} is the frequency at which the value of ϵ'' is maximum. The values of $\epsilon_0 - \epsilon_\infty$ were obtained from the Cole circular-arc type of plot[11] or the area under the ϵ'' vs. $\log f$ curve.[12] For PVAc, PS, and PMMA, $(\epsilon_0 - \epsilon_\infty)$ increases slightly with decreasing temperature. It may be permissible to consider the value of $ng\mu^2$ in these polymers as nearly independent of temperature, since $\epsilon_0 - \epsilon_\infty$ is explicitly proportional to $1/T$, as was shown in eq. (2).

T_g of PVAc is $30°C$., by our volume expansion measurement, and f_{max} of this polymer is about 10^{-2} cycles/sec. at $30°C$. At temperatures below $30°C$., f_{max} becomes much lower, but $ng\mu^2$ remains nearly constant. From this result, it is suggested that the chain segments move very slowly but never stop moving at temperatures below $30°C$. (at least down to $13.2°C$.); that is, the T_g determined from the ϵ''-vs.-temperature curve at a constant frequency of 10^{-4} cycles/sec. is about $20°C$., which is $10°C$. lower than the T_g determined by the usual physical experiment. It has been reported[13] that T_g of PS and PMMA are $100°C$. and $72–105°C$., respectively. Also, in the case of the two polymers,
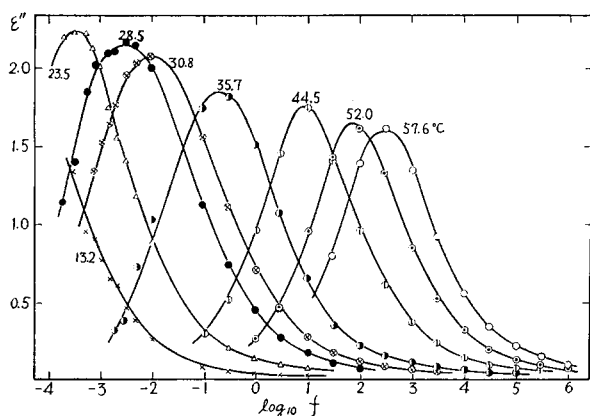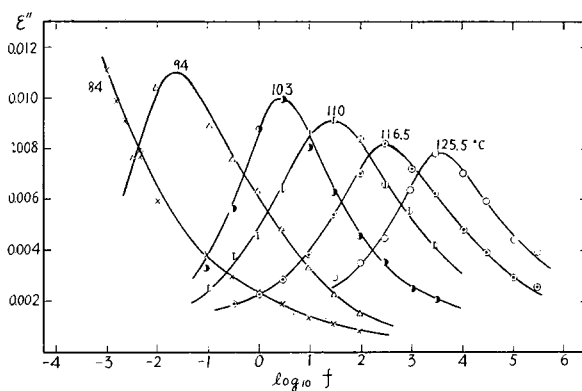
Fig. 1. Dielectric loss of PVAc.
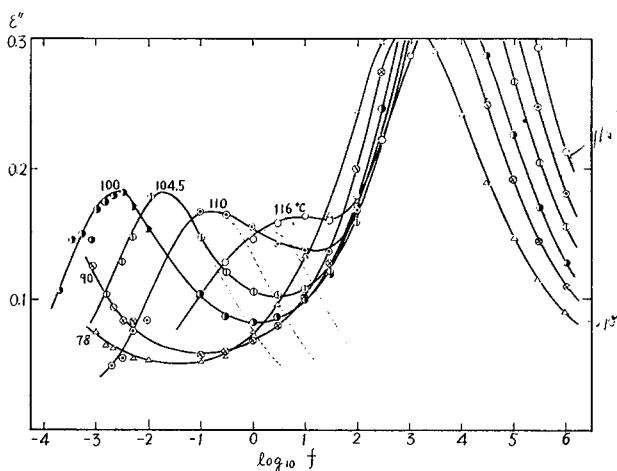

Fig. 2. Dielectric loss of PS.
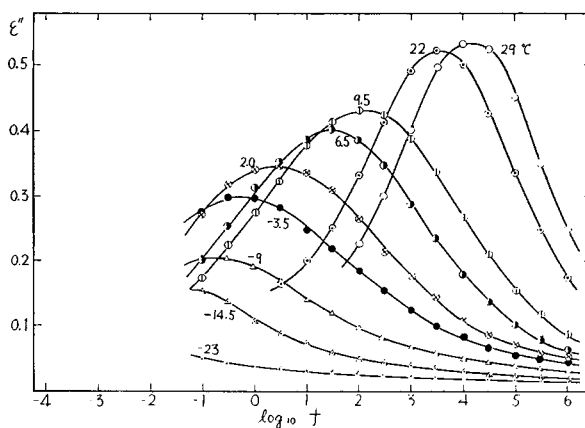

Fig. 3. Dielectric loss of PMMA.

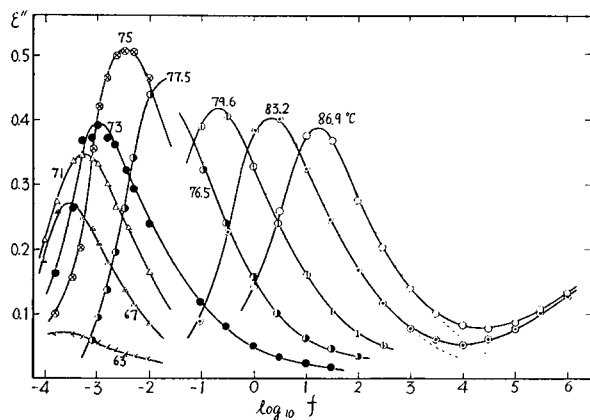Fig. 4. Dielectric loss of PVDC.

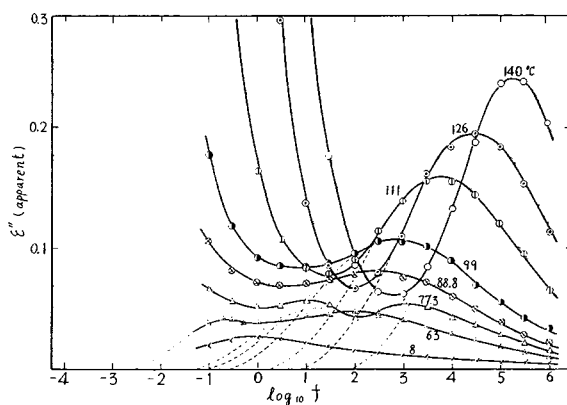
Fig. 5. Dielectric loss of PET.

Fig. 6. Dielectric loss of PAN.

if T_g is determined from the ϵ'' vs. temperature curve at very low frequency, it becomes considerably lower than T_g by the usual experiment. Kauzmann[14] indicated that the relaxation time for dielectric polarization is of the order of several minutes to

an hour at the T_g, determined by the thermal expansion or the specific heat. For PVAc, PS, and PMMA, the results similar to Kauzmann's findings are obtained, and hence the molecular processes involved in the glass transition seem to be a relaxa-
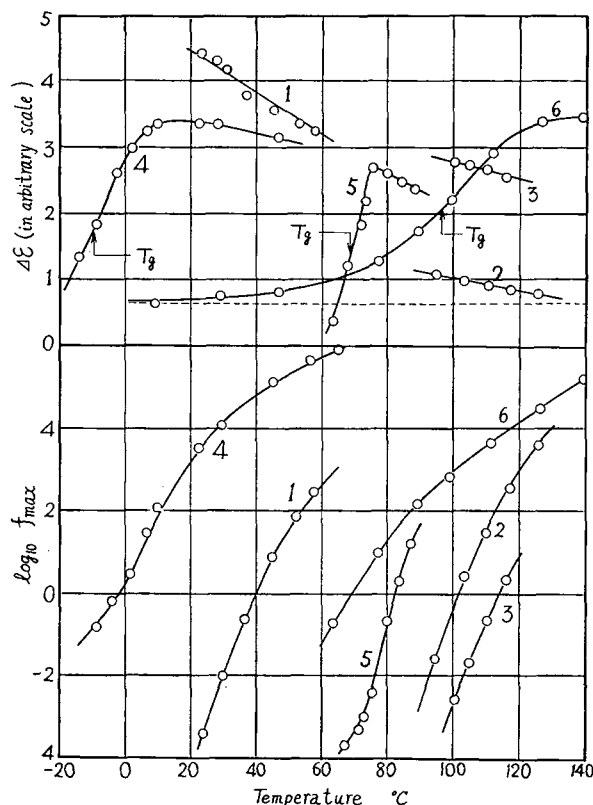
Fig. 7. Temperature dependences of the positions and the magnitudes of the dielectric absorptions: (1) PVAc; (2) PS; (3) PMMA; (4) PVDC; (5) PET; (6) PAN.

tion processes. The same suggestion is obtained from the volume relaxation experiment described in the following section.

On the other hand, in PVDC, PET and PAN, not only does f_{max} shift towards low frequency with decreasing temperature, but $\epsilon_0 - \epsilon_\infty$ decreases steeply in certain temperature ranges. For PVDC, the transition range of $\epsilon_0 - \epsilon_\infty$ is the temperature range of $+10$ to $-30°$C. If we define the transition temperature as that at which the value of $\epsilon_0 - \epsilon_\infty$ is half of the maximum value, we obtain $-10°$C. T_g of PVDC by our volume expansion experiment is $-11°$C. The transition temperature of $\epsilon_0 - \epsilon_\infty$ coincides with T_g by volume expansion. In a previous paper,[15] it was confirmed that the cooling rate has only a little effect on the transition of $\epsilon_0 - \epsilon_\infty$. Decrease of $\epsilon_0 - \epsilon_\infty$ means decrease of $ng\mu^2$, as is evident from eq. (2). It is supposed that the decrease of $\epsilon_0 - \epsilon_\infty$ is due to either of the following factors: (1) polar groups which can be rotated at temperatures higher than T_g are frozen and cannot be rotated at temperatures lower than T_g; or (2) relative arrangements of polar groups in segments are suddenly changed and residual polar-

ity is diminished at temperatures lower than T_g. In either case, the decrease of $\epsilon_0 - \epsilon_\infty$ is due not to a relaxation process but to an essential change in molecular arrangements. If we determine T_g of PET and PAN by the transition of $\epsilon_0 - \epsilon_\infty$, we obtain 68°C. and 96°C., respectively. Undoubtedly, PAN has a small constant value of $\epsilon_0 - \epsilon_\infty$ in the low temperature range, as was shown in Figure 7. It is due to the absorption located in the high frequency region in Figure 6 which can be observed at temperature below T_g but also creeps into the low frequency absorption at higher temperature. It was indicated in a previous paper[8] that for polychlorotrifluoroethylene, the $\epsilon_0 - \epsilon_\infty$ transition was observed and the transition temperature was $-20°$C.

From the above considerations, it is suggested that the glass transition of these polymers is an essential one which includes a small relaxation effect. A similar conclusion is suggested by the volume relaxation experiments described in the following section. From the dielectric point of view, so-called glass transitions of polymers may be divided into the apparent relaxation transition and the transition itself, which includes a small relaxation effect. It is an interesting fact that the transitions of the amorphous polymers are of the former type and those of the crystallizable polymers are of the latter type. This would not be due to the existence of the crystallites, since the PET sample has a density of 1.339 and is amorphous, as shown by x-ray studies.

Dilatometric Data

We chose PVAc and PVDC as the representative samples among six polymers. Volume vs. temperature curves of the two polymers are shown in Figure 8. T_g of PVAc and PVDC by this experiment are 30°C. and $-11°$C., respectively. The volume vs. time curves are shown in Figures 9 and 10. T_s of PVAc and PVDC were 55°C. and 18°C., respectively.

In PVAC, at a temperature T_r exceeding T_g by about 10°C., temperature and volume equilibria appeared to be attained simultaneously. At T_r above T_g, the volume equilibrium was attained within a comparatively short time. However, at T_r below T_g, the volume did not reach the equilibrium condition within 600 min. Arrow lines in Figure 8 represent the volume changes with time and a, b, c, etc., represent equilibrium values of the volume or the values after 600 min. when equilibrium was still not attained. This result suggests
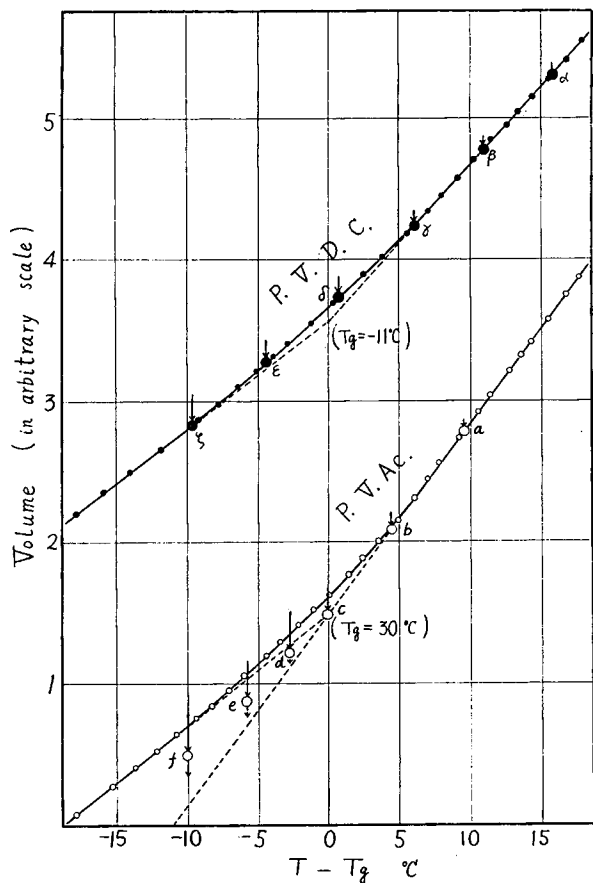
Fig. 8. Temperature dependences of the volumes of PVAc and PVDC.

that the slower the cooling rate, the lower is T_g, and finally the transition seems to disappear.

In PVDC, on the other hand, volume equilibrium appears to be obtained within 600 min. at T_r above $-20.5°C$. The rate of volume relaxation is lowered with decreasing temperature. Equilibrium values of the volume are represented by α, β, γ, etc., in Figure 8 and lie along the volume vs. temperature curve obtained at a cooling rate of 0.3°C./min. This result implies a thermodynamic transition.

Thermodynamic Data for Dielectric Relaxation Process

A phenomenological approach to the nature of the glass transition of polymer was taken in a previous section. Another important problem is the study of the molecular process involved in the transition. However, since our present results are imperfect for such a purpose, we merely show the apparent activation energy ΔH^* for the dielectric relaxation process.

The results are shown in Figure 11. All values were calculated by Kauzmann's method.[16] ΔH^* for six polymers shows strong temperature dependence, see Figure 11. In PVDC and PET, ΔH^* increases with decreasing temperature as the transition range is approached, becomes maximum at a temperature a little higher than T_g, and then decreases with decreasing temperature. This behavior may involve volume and energy requirements for local cooperative motions. We studied the dielectric behavior of PET of various degrees of crystallinity and found that, the higher the degree of crystallinity, the lower is the activation energy.[17] Possibly the decrease of ΔH^* in the transition range would be due to the increase of regions rigid in structure in which the molecular responses to electrical sinusoidal stress are similar to those in crystalline region. In PAN, the peak of ΔH^* is not clearly observed. Since ΔH^* is affected by another loss process located in higher frequency region, the situation may be complicated.

ΔH^* for the three uncrystallizable polymers increases with decreasing temperature as T_g is approached and does not pass through a maximum.
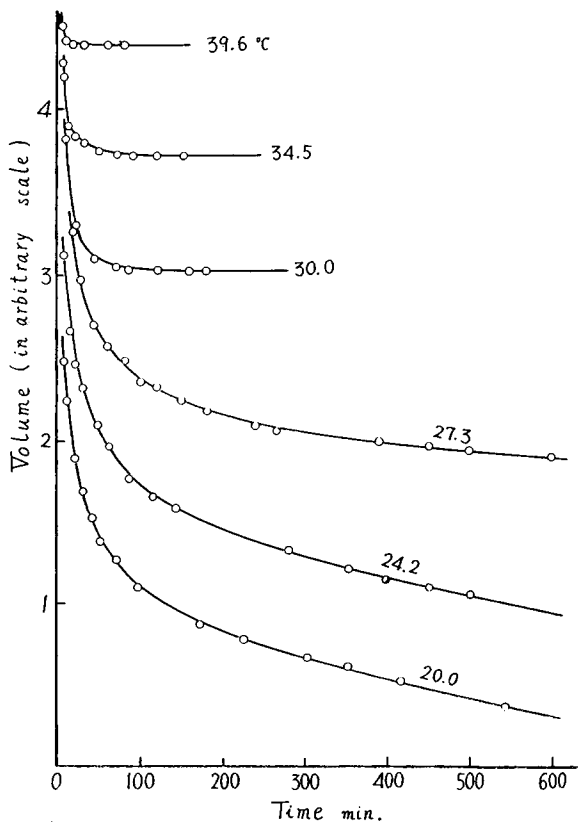

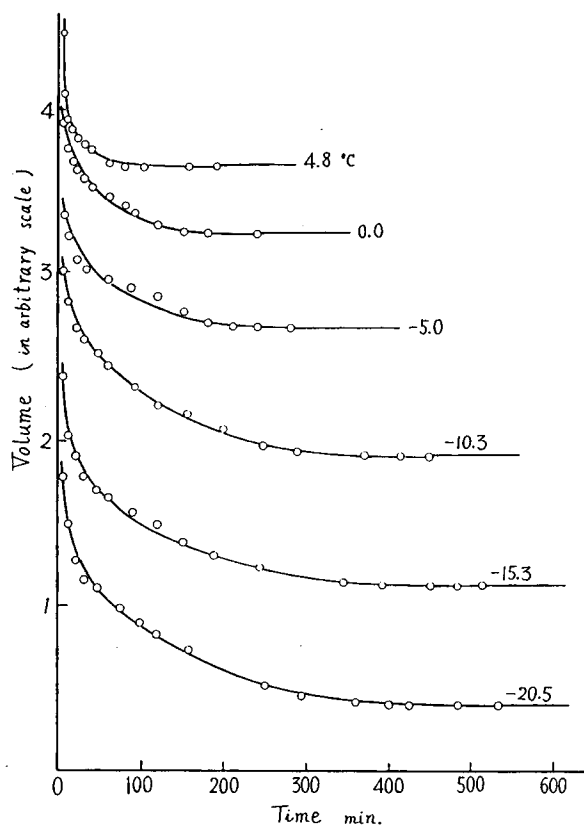Fig. 9. Volume vs. time curves at various temperatures for PVAc.

Fig. 10. Volume vs. time curves at various temperatures for PVDC.

ΔH^* vs. temperature curves are sigmoidal forms which are different from the curve resulting from the equation of Williams, Landel, and Ferry.[18]

CONCLUSIONS

ϵ'' for six polymers in the glass transition ranges have been measured over a wide frequency range, and two distinctive absorptions have been observed. In PVAc or PS or PMMA, the absorption exists at frequencies of 10^{-2} to 10^{-3} cycles/sec. at
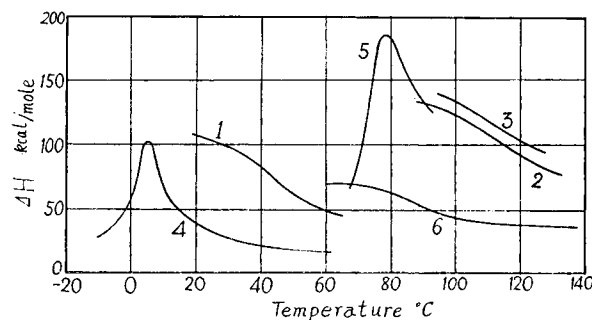

Fig. 11. Temperature dependences of the activation energies for the dielectric relaxations: (1) PVAc; (2) PS; (3) PMMA; (4) PVDC; (5) PET; (6) PAN.

the T_g determined by ordinary physical experiment, and shifts towards lower frequency at lower temperature; the magnitude of absorption is almost independent of temperature. The volume relaxation experiment suggests that T_g disappears when equilibrium is reached. Therefore, the glass transitions of these uncrystallizable polymers are considered as apparent only. For PVDC, PET and PAN, on the other hand, the absorption magnitude, which is independent of frequency, decreases steeply with decreasing temperature in the glass transition range. T_g determined from the temperature dependence of the magnitude coincides with that from the volume expansion. Volume relaxation experiments suggest that T_g remains when equilibrium is reached. Therefore, the glass transitions of these crystallizable polymers are considered as essential. Temperature dependences of ΔH^* for the dielectric relaxations of these crystallizable polymers are different from those of the uncrystallizable polymers. The glass transition behavior of polymers is considered to fall into one of two types, depending on the structure, at least for the six polymers studied here.

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Synopsis

Glass transition phenomena in several polymers were studied by dielectric and dilatometric measurements. The dielectric measurements were made over the frequency range of 10^{-4} or 10^{-1} to 10^6 cycles/sec. and the temperature range of the glass transition. In the dilatometric study, volume relaxation curves and volume vs. temperature curve were obtained. The transition in three amorphous polymers, (polyvinyl acetate, polystyrene, and polymethyl methacrylate), depends upon frequency or rate of cooling and seems to be an apparent transition. In three crystallizable polymers, (vinylidene chloride–vinyl chloride copolymer, polyethylene terephthalate, and polyacrylonitrile), the magnitude of the dielectric absorption decreases steeply with decreasing temperature in the transition range, and the transition by the volume expansion remains when equilibrium is attained. The transition in the three crystallizable polymers seems to be a real one. Temperature dependences of the activation energies of the dielectric relaxation processes have been described.

Résumé

Le phénomènes de transition vitreuse de plusieurs polymères ont été étudiés par des mesures diélectriques et dilatométriques. Les mesures diélectriques étaient faites sur une gamme de fréquence de 10^{-4} ou 10^{-1} à 10^6 cycles/sec. et un domaine de température voisin de la transition vitreuse. Dans l'étude dilatométrique on a établi les courbes de volume/rélaxation et volume/température. La transition de trois polymères amorphes, acétate de polyvinyle, polystyrène et polyméthacrylate de méthyle, dépend de la fréquence ou de la vitesse de refroidissement, et semble être une transition apparente. Dans trois polymères cristallisables, copolymères de chlorures de vinylidène et de vinyle, le téréphthalate de polyéthylène et le polyacrylonitrile la grandeur de l'absorption diélectrique décroît rapidement avec une diminution de température dans le domaine de la transition, et la transition au cours de l'expansion de volume se maintient lorsque l'équilibre est établi. La transition dans les trois polymères cristallisables semble être essentielle. La dépendance thermique des énergies d'activation des processus de rélaxation diélectrique a été décrite.

Zusammenfassung

Die Erscheinung der Glasumwandlung wurde bei einigen Polymeren mittels dielektrischer und dilatometrischer Messungen untersucht. Die dielektrischen Messungen wurden über den Frequenzbereich von 10^{-4} oder 10^{-1} bis 10^6 Hertz und im Temperaturbereich der Glasumwandlung ausgeführt. Bei der dilatometrischen Untersuchung wurden Volumrelaxationskurven und Kruven für die Temperaturabhängigkeit des Volumens erhalten. Bei drei amorphen Polymeren, Polyvinylacetat, Polystyrol und Polymethylmethacrylat, hängt die Umwandlung von der Frequenz oder Geschwindigkeit der Abkühlung ab und es dürfte sich dabei um eine scheinbare Umwandlung handeln. Bei drei kristallisierbaren Polymeren, dem Copolymeren von Vinylidenchlorid und Vinylchlorid, Polyäthylenterephthalat und Polyacrylnitril nimmt im Umwandlungsbereich die Grösse der dielektrischen Absorption sehr rasch mit fallender Temperatur ab und die durch die Volumsexpansion gemessene Umwandlung bleibt bei Erreichung des Gleichgewichts erhalten. Bei den drei kristallisierbaren Polymeren scheint as sich um eine echte Umwandlung zu handeln. Die Temperaturabhängigkeit der Aktivierungsenergien der dielektrischen Relaxationsvorgänge wurde beschrieben.