

Diffusion of Ethyl Methyl Ketone in Gamma-Ray Irradiated Polystyrene

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Integral absorptions and desorptions of ethyl methyl ketone in gamma-ray irradiated polystyrene were studied as a function of film thickness at a temperature below the glass transition point. For the slightly-crosslinked polystyrene, in all cases investigated the effect of sample thickness existed and the initial slopes of the reduced absorption curves increased with increasing film thickness, though the individual absorption and desorption curves appeared to have the shape expected from the purely Fickian mechanism. The values of the mutual diffusion coefficient, D , of the system were calculated by using the method proposed by Odani et al. and were compared with those for untreated polystyrene. It was found that the values of D for the slightly-crosslinked polystyrene are somewhat greater than those for the untreated one in the concentration region studied. A tentative explanation of these results were given in terms of the function of intra- and inter-molecular crosslinks introduced by the gamma irradiation. For the highly-crosslinked polystyrene all the absorption and desorption curves were of non-Fickian type in the concentration region studied. This anomalous behavior was interpreted in terms of the model proposed by Long and Richman.

INTRODUCTION

It is now well established that absorption and desorption processes of organic vapors in amorphous polymer solids which are in the glassy state are quite different from those in amorphous polymer solids which are at temperatures well above the glass transition temperatures, T_g . For the latter condition the processes are of the Fickian type; that is, the diffusion coefficient being a function of penetrant concentration alone and a constant surface concentration being maintained during absorption or desorption. But at temperatures below T_g they exhibit various deviations from Fickian features, and they are usually called non-Fickian or anomalous processes.

To distinguish between Fickian and non-Fickian diffusion two criteria have usually been used. One is that for the initial stage of absorption or desorption a plot of weight of vapor takeup or loss, M_t , at time t versus \sqrt{t} should be linear if diffusion follows Fick's law with the above-cited conditions. A second criteria is that above the linear portions the plots of M_t versus \sqrt{t} are always concave against the \sqrt{t} axis.

According to these criteria, in systems amorphous polymer + organic vapor the absorption process changes from non-Fickian type to Fickian type in the vicinity of a penetrant concentration at which the given polymer-vapor mixture undergoes

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glass transition at the temperature of the experiment. This concentration is referred to as the critical concentration.^{1,2)}

In previous papers^{3,4)} it has been shown that for the systems polystyrene+organic vapors the effect of film thickness still exists in the concentration region slightly above the critical concentration, though the individual absorption curves fulfill the above-mentioned criteria; that is, absorption data from varying thickness experiments can not be reduced to a single curve when M_t/M_∞ is plotted against \sqrt{t}/l , where M_∞ is the value of M_t at absorption equilibrium and l is the thickness of film. This is also the case for desorption experiments. It has been shown that in the concentration region studied the initial slopes of the M_t/M_∞ versus \sqrt{t}/l plots increase with increasing film thickness. This was interpreted as being due to slow change of polymer structure accompanying diffusion even in the region of penetrant concentrations where the given mixture is considered to be in the non-glassy state and the absorption and desorption processes are not altogether controlled by the purely Fickian mechanism. However, no definite information has as yet been obtained about the behavior in the concentration region somewhat above the critical concentration, because uncrosslinked polystyrene films can not support their own weight from spring balance and it is not able to perform the absorption experiments.

In order to obtain some more information about the diffusion of organic vapor in amorphous polymer in the region of relatively high concentration of penetrant, we here study by using various film thicknesses the absorption and desorption of ethyl methyl ketone in atactic polystyrene which is crosslinked slightly by the gamma irradiation. The effect of crosslinking upon the diffusion process is also examined with highly crosslinked polystyrene.

EXPERIMENTAL

Materials

Polystyrene (PS) used in the present study was prepared by thermal polymerization without catalyst in our laboratory. It was purified by precipitation from a 2% benzene solution by addition of methanol. The viscosity-average molecular weight estimated by Flory's equation⁵⁾ was 1.27×10^6 . Films of the polymer were obtained by slow evaporation of solvent from 1.5% methylene chloride solution cast on a clean mercury surface. Final traces of the casting solvent were removed by leaching in methanol for more than a week, followed by drying in a vacuum oven at 50°. The film thickness was determined from the known weight and area, using a value 1.05g./ml. for the density of PS. The films used for sorption measurements were approximately 0.6, 0.9, 1.2, 1.5, and 1.8×10^{-2} cm. thick.

The gamma irradiations of PS films were performed in nitrogen atmosphere at a room temperature using the Co⁶⁰ irradiation facility of the Institute for Chemical Research, Kyoto University. It has been reported that the crosslinking occurs preferentially under this condition.⁶⁾ The dose rate was approximately 1.2×10^5 r./hr.. In Table 1 are summarized the intrinsic viscosities of the irradiated PS films in benzene at 30° and the penetrant concentration region studied. It is seen that films 1 and 2 can be dissolved in benzene at 30° but film 3 can not.

Hereafter we designate the former two as slightly-crosslinked PS and the latter highly-crosslinked PS.

Table 1. The irradiated PS films used in diffusion studies.

Film No.	Radiation dose megarep	$[\eta]$ dl./g.	EMK concentration studied g.EMK/g.PS
U	0	3.38	—
1	5.1	2.29	0.14~0.29
2	10.2	3.36	0.14~0.29
3	60.5	Insoluble	0.19~0.54

The ethyl methyl ketone used was of G. R. grade. No attempt was made to effect further purification.

Apparatus and Procedure

The sorption apparatus used was practically the same as that reported elsewhere.¹³

The integral absorption and desorption technique was employed; that is, a given polymer film was suspended from a sensitive quartz spring in a sorption tube and was equilibrated with the vapor of EMK at a desired pressure P_1 . Then the pressure was suddenly increased to a higher pressure P_2 and the absorption process was followed by measuring the extension of the spring as a function of time. After the film has reached equilibrium with the surrounding vapor at a pressure P_2 , the pressure of the sorption tube was suddenly reduced from P_2 to P_1 and the resulting desorption process was measured as in the case of absorption. This absorption-desorption run was carried out with several different values of $\Delta P = P_2 - P_1$. All the measurements were carried out at 25°. This temperature is well below the glass transition temperature of the polymer.¹³

RESULTS AND DISCUSSION

Slightly-crosslinked PS+EMK

Absorption isotherm data for the two slightly-crosslinked PS samples at 25° are given in Fig. 1. Here the ordinate represents the mass of EMK in grams per gram of a given polymer at dry state and the abscissa the relative pressure of ambient vapor. The corresponding data for the system uncrosslinked PS+EMK at the same temperature are included in the figure for comparison. We see that all the data fall satisfactorily on a single curve. Thus it may be concluded that at small irradiation doses the effect of crosslinking does not change the solubility of EMK in PS.

Figure 2 shows the typical absorption data for slightly-crosslinked PS+EMK at 25° and from the initial concentration $C_i = 0.24$ g./g. To avoid confusion, only partial data are presented. Here M_t is the amount of EMK absorbed per gram of dry polymer at time t , M_∞ the value of M_t at absorption equilibrium, and l the thickness of film. It is seen from the Fig. 2 that absorption curves are initially linear and this linearity holds over about 60% of the total concentration increment. Above the linear regions absorption curves are concave against the time axis.

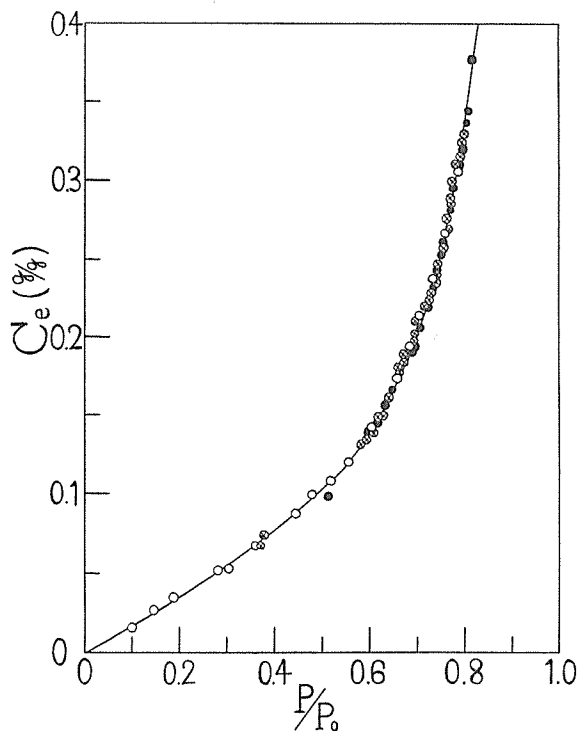


Fig. 1. Absorption isotherms of slightly-crosslinked and uncrosslinked PS + EMK at 25°.

Slightly-crosslinked PS:	Film 1	⊗
	Film 2	●
Uncrosslinked PS:	Film U	○

However, it is also seen that the absorption plots can not be reduced to a single curve; the initial slopes of absorption plots increase with increasing film thickness. This is also the case for the paired desorption to the final concentration $C_r=0.24$ g./g. A similar trend was observed for all results at other initial concentrations studied. These results imply that even in the region of relatively high concentration of penetrant the diffusion of penetrant does not follow the purely Fickian mechanism.

Kishimoto and Matsumoto⁹ have recently shown similar effect of film thickness upon the absorption and desorption kinetics of organic vapors in amorphous polymers when the measurement is made at temperatures slightly above T_g . They have also shown that the thickness anomaly is vanished at a temperature about 20° above T_g . For the system studied here it is estimated that the critical concentration corresponding to the temperature of the experiment is 0.14 g./g. Therefore, it may be supposed that at the highest initial concentration studied (0.29 g./g.) the mixture would be in the rubbery state. This is supported by the data obtained from tensile creep measurements of the system; in this concentration region the values of creep compliance show that the mixture is in the rubbery state. Nevertheless, the absorption and desorption processes exhibited the film thickness effect. This appears to suggest that the effect of increasing penetrant concentra-

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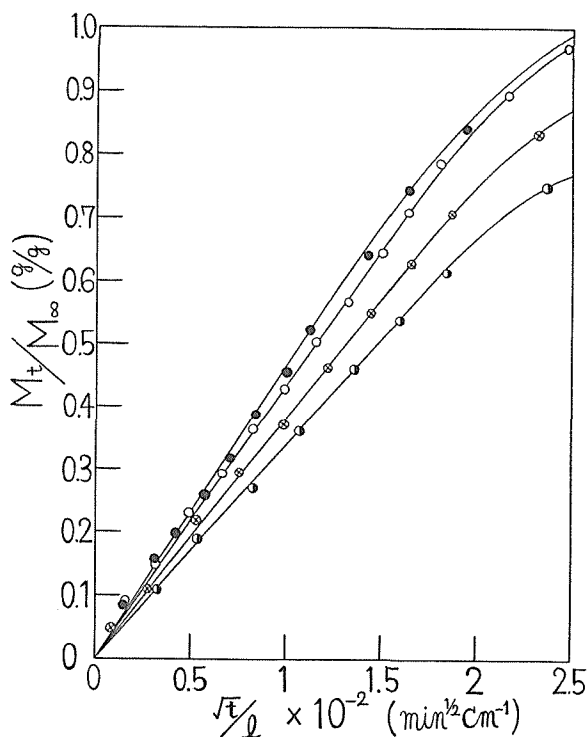


Fig. 2. Absorption curves for EMK in film 1 at 25°. Initial concentration $C_i=0.24$ g./g.

	l 10^{-2} cm.	
Concentration difference	1.823	●
$\Delta C=0.035$ g./g.	1.505	○
	1.114	⊗
	0.985	◐

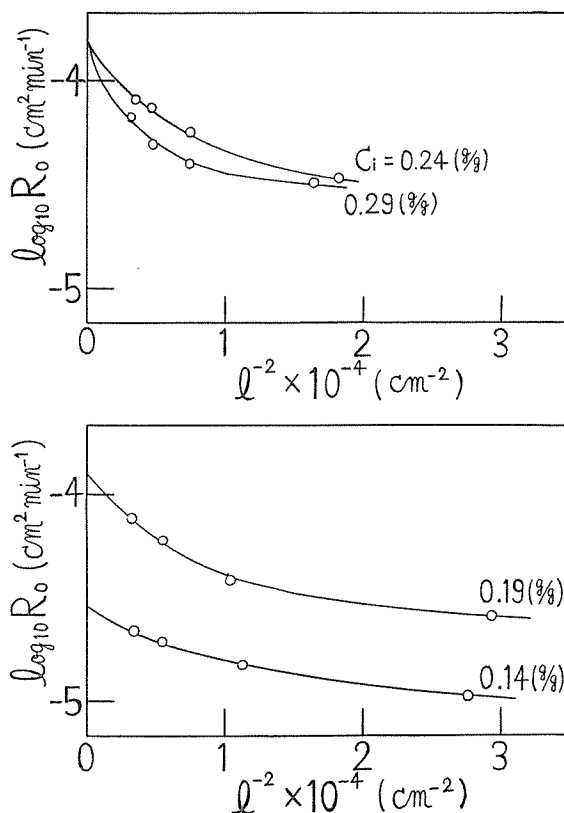
tion may not exactly be equivalent to that of rising temperature.

Recently it has been shown that the mutual diffusion coefficient, D , of a given system can be evaluated by the following procedure ⁴: that is,

- (1) Plot M_t/M_∞ against $\sqrt{t/l}$, and obtain R from each curve, where R is the value of t/l^2 at $M_t/M_\infty=0.5$;
- (2) Plot R against concentration difference $\Delta C=C_f-C_i$ with C_i and l as parameters, and extrapolate to zero value of ΔC to give R_0 ;
- (3) Plot R_0 against l^{-2} for each C_i and extrapolate to zero value of l^{-2} to give R_i ;
- (4) Multiply R_i by the factor $\pi/64$, and then D is evaluated as a function of C_i alone.

In Figures 3a and 3b the values of R_0 for film 2 are plotted semi-logarithmically against l^{-2} at $C_i=0.14, 0.19, 0.24,$ and 0.29 g./g. It is seen that the higher the initial concentration the steeper the slope of the plot, and the dependence of R_0 on film thickness is more marked than that of corresponding plot for the system uncrosslinked PS+EMK shown in Fig. 4. Although the results for film 1 are not given here, the plots are very similar to those for film 2.

The values of D evaluated by the above method are plotted semi-logarithmically



Figs. 3a, 3b. Logarithmic correlation plots of R_0 and l^{-2} for EMK in film 2 at 25°.

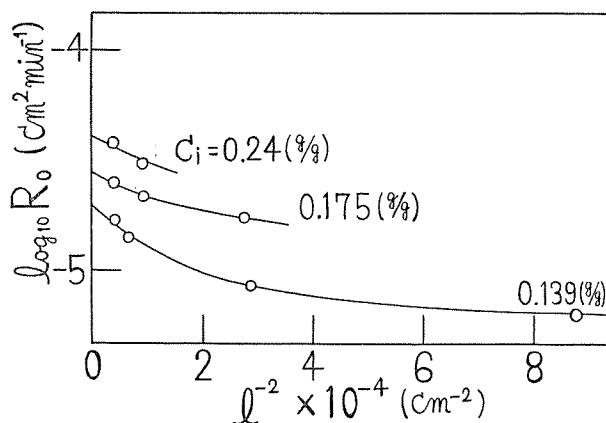


Fig. 4. Logarithmic correlation plots of R_0 and l^{-2} for EMK in film U at 25°.

against penetrant concentration in Fig. 5 together with those for uncrosslinked PS film evaluated in the previous study.⁴⁾ It is of particular interest and rather puzzling that in the concentration region studied D is actually greater for slightly crosslinked PS's than it is for uncrosslinked PS, since it might be anticipated that

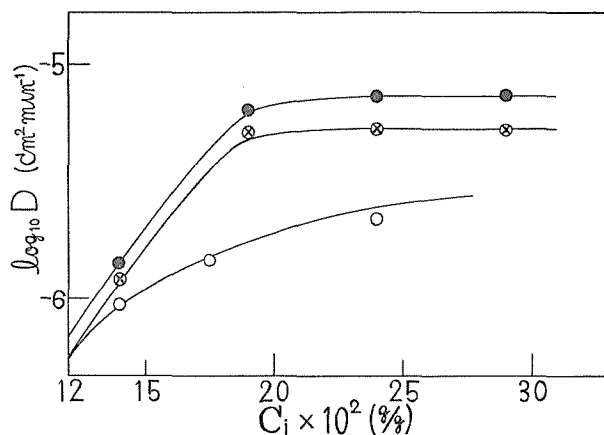


Fig. 5. Logarithmic correlation plots of mutual diffusion coefficient D and initial concentration C_i for slightly-crosslinked and uncrosslinked PS+EMK at 25°.

Film 1: \otimes
 Film 2: \bullet
 Film U: \circ

the values of D would decrease with introduction of crosslinks in the polymer matrix by the gamma irradiation. The similar behavior has been observed for diffusion of low molecular weight compounds in vulcanized rubber.^{9,10}

As mentioned before, at small irradiation dose the effect of crosslinking does not change the solubility of EMK in PS. Therefore the chemical potential whose gradient is the driving force to the mass flux in the isothermal system does not appear to have been changed by crosslinking. There must be some other forces produced by crosslinking.

Suppose one molecule of the penetrant diffuses into polymer film. This process must be accompanied by a local cooperative movement of several polymer segments. This type of local rearrangement of polymer segments will not be influenced so much by whether polymer is crosslinked or not, provided that the degree of crosslinking is kept at a low level. However, if there exist intramolecular or intermolecular crosslinks, the resulting movements of the whole chain caused by the movements of segments will be accelerated by intramolecular crosslinks, and also readily transmitted to another chains through intermolecular crosslinking points. As it is supposed that the direction of the movements are to be in the opposite direction to the flux of the penetrant caused by the chemical potential gradient, the vapor may penetrate into crosslinked polymer more rapidly than into uncrosslinked one.

Finally, it should be mentioned about the effect of the main-chain breakdown caused by the gamma irradiation. Table 1 indicates that the intrinsic viscosity of the irradiated film is lower than that of untreated film.* This may be caused not only by the incompleteness of replacing air with nitrogen, but also by the

* However, it was found that the dissolution rate of untreated PS in benzene is much higher than those of irradiated PS's. This may suggest that crosslinking has preferentially occurred in our samples.

intramolecular crosslinking. For the former effect it has been reported that a slight amount of remaining oxygen can attack polymer chains and produce main-chain breakdown.¹¹ For the latter, viscosity may be regarded as the measure of the dimensions of one polymer chain and intramolecular crosslinking can reduce the dimensions. As the infrared spectra of film 1 and 2 showed no new peaks indicating the occurrence of scissions compared with that of PS without irradiation, it can not be supposed that scissions have occurred so much. As the number of scissions is decided only by the amount of remaining oxygen, the molecular weight of film 2 would be larger than that of film 1. Thus, it may be considered due to cross-linking that the values of D increase with increasing irradiation dose, and can be believed that the qualitative explanation mentioned above is probably correct.

Highly-crosslinked PS+EMK

In the concentration region studied all the absorption and desorption curves for film 3 were sigmoid as will be shown later. Thus, from the absorption experiments, it was not able to evaluate the value of D as in the case for film 1 and 2. This may be expected from the data shown in Table 1, that is, for film 3 the degree of crosslinking is so high that the film can not be desolved into benzene, and the absorption rate of penetrant may decrease markedly with increasing crosslinking due to restraint introduced into the chain molecules.

If it is assumed that this effect of high degree of crosslinking upon the absorption rate is interpreted in terms of the concept of the time dependence of surface concentration, then we may obtain the non-Fickian type absorption curves by solving the general form of Fick diffusion equation,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right), \quad (1)$$

with a variable surface concentration and D is a function of C alone, where x is the space coordinate measured in the direction of diffusion. That is, the surface concentration will gradually approach an equilibrium value at a finite rate which may depend upon the rate of relaxation of polymer chains. The qualitative evidence of the slow change of surface concentration will be obtained from the comparison of the rate of absorption with that of paired desorption at a certain initial concentration. That is, it is observed for the system above $C_i=0.19$ g./g. that initial rate of absorption for a given pressure interval is always lower than those for paired desorption. Since there is no evidence that the diffusion coefficient of the system ever decrease with increasing concentration, the only possible explanation may be that the equilibrium surface concentration are established at a slow rate.

The expression for the time dependence of surface concentration C_s assumed here in solving the diffusion equation was the same as that used by Long and Richman¹²⁾ who succeeded to derive both sigmoid and two-stage absorption curves, which have been observed for a number of glassy polymer-penetrant systems. Thus

$$\begin{aligned} C_s &= C_i && \left(-\frac{l}{2} < x < \frac{l}{2}, t=0 \right) \\ C_s &= C_0 + (C_r - C_0)(1 - e^{-\beta t}) && \left(x = \pm \frac{l}{2}, t > 0 \right) \end{aligned} \quad (2)$$

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where C_0 is a parameter and is assumed for absorption to be greater than the initial concentration C_i , and β is a parameter. Furthermore, on performing calculation we have assumed a constant D as the zeroth approximation, because the diffusion equation can not be solved for the general case of a diffusion coefficient which depends on concentration. It has demonstrated PS+EMK that the values of D obtained from permeation data change slightly with concentration in the concentration region above $C_i=0.19$ g./g.¹³⁾ Thus it does not seem a bad approximation to replace the concentration dependent diffusion coefficient by a constant D in the concentration range studied.

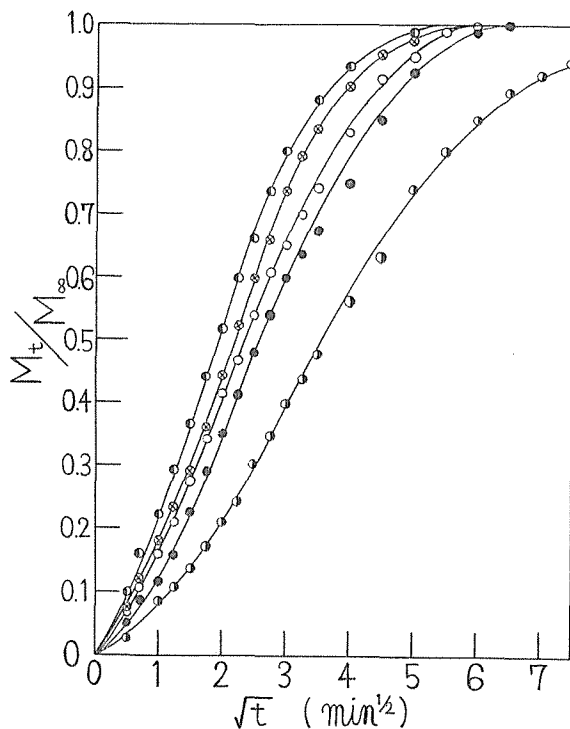


Fig. 6. Absorption curves for EMK in film 3 at 25°. Concentration difference $\Delta C=0.10$ g./g., film Thickness $l=1.505 \times 10^{-2}$ /cm.

Experimental:	C_i , g./g.	
	0.19	⊙
	0.24	⊗
	0.34	○
	0.42	◐
	0.54	●
Calculated:		—

Table 2. The values of parameters for each initial concentration C_i used in the calculation.

C_i , g./g.	0.19	0.24	0.34	0.42	0.54
$\frac{C_0 - C_i}{C_\infty - C_i}$	0.55	0.50	0.50	0.50	0.28
β , min ⁻¹	0.90	0.30	0.17	0.10	0.05

The solution to the diffusion equation then may be expressed by the following equation¹²⁾;

$$\begin{aligned} \frac{M_t}{l\rho_0} = & (C_0 - C_i) - \frac{8(C_0 - C_i)}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-D(2n+1)^2\pi^2 t/l^2}}{(2n+1)^2} \\ & + (C_f - C_0) - (C_f - C_0) e^{-\beta t} \left(\frac{2D}{\beta l} \right)^{1/2} \tan \left(\frac{\beta l^2}{4D} \right)^{1/2} \\ & - \frac{8(C_f - C_0)}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-D(2n+1)^2\pi^2 t/l^2}}{(2n+1)^2 \left[1 - (2n+1)^2 \left(\frac{\pi^2 D}{\beta l^2} \right) \right]} \end{aligned} \quad (4)$$

where ρ_0 is the density of dry polymer. The experimental data and the results from the calculation are shown in Fig. 6, and the values of parameters used in the calculation are listed in Table 2. The agreement between the calculated curves and experimental data is quite good. However, it should be emphasized that this explanation as well as the specific interpretation of the parameters is rather speculative and further experiments, such as a micrographic study, are needed to confirm it.

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