# Modeling of Mass Transfers between Food Simulants and Treated Plasticized PVC

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**ABSTRACT:** PVC is often used in food packaging and blood bags. This study concerns mass transfers between plasticized PVC, having been subjected to a treatment, and liquid food or food simulants. The treatment reduces the diffusion of the plasticizer and the influence of some factors of this processing are investigated. A mathematical model, able to simulate these mass transfers and to quantify the treatment parameters, is proposed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 49–58, 1999

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### INTRODUCTION

Plastic materials are increasingly used in food packaging. Unfortunately, when a plastic is in contact with food, a migration of the components of plastics may occur. The additives, such as antioxidants, antistatic agents, lubricants, or plasticizers represent one of the main sources of contamination of packaged food. In addition, these losses of additives influence the physical properties and performances of plastic materials.<sup>1</sup>

Migration behavior has attracted considerable legislative attention and most of the existing regulations stipulate that packaging materials must not alter the quality of the food.<sup>2,-5</sup> To simplify the tests, it is possible to use food simulants. According to the European Communities regulations, the detection and quantification of contaminants migrating from the polymers into fatty food simulants are essential for the safety assessment of plastic packaging materials in contact with food.

Plasticized PVC is one of the plastic materials often used in the packaging of liquid foods and blood. Generally, a simultaneous transfer of the liquid into and the plasticizer out of the PVC takes  $place^{6,-8}$  with the following results: The liquid food is contaminated by the plasticizer and there is a decrease in the mechanical properties of the polymer.

It is possible to prepare plasticized PVC exhibiting low mass transfer.<sup>6,9</sup> The first work on this topic was described in the thesis by Taverdet (1985).<sup>6</sup> It is a two-step process:

- (i) Plasticized PVC (with diethylhexyl phtalate or DEHP) is immersed in a liquid for a short time (e.g., 2 min).
- (ii) Then, the PVC is extracted from the liquid and dried. During this step (5 min), a part of the liquid located in the PVC evaporates.

With the PVC treated in this way, the transfer of plasticizer is considerably reduced.

Our investigations have shown that the decrease of mass transfer from pretreated PVC is strongly dependent on several parameters: the time and temperature of soaking during the first step, the temperature, and the time of drying. The efficiency of the process is also a function of the initial plasticizer concentration of the original PVC.

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The nature of the liquid in which PVC is immersed during the first stage is also an important factor because with some liquids there is no effect. Since 1985, many articles have been published on this topic,<sup>10–12</sup> but no one has quantified the importance of these factors and no one has given a satisfactory explanation concerning the reduction of mass transfer in this case.

The main purpose of this article was to study some factors having an important influence on this process and to propose a model that allows a simulation of the reduction of mass transfers. Therefore, it will be possible to quantify the diffusion rate in terms of an average diffusion coefficient.

#### EXPERIMENTAL

#### Materials

The analyses of DEHP in the liquid were performed by gas chromatography (Intersmat IGC 16) after an addition of diethylhexyl adipate as the internal standard. The stationary phase is Chromosorb Q and 2.5% OV 17 silicone rubber (Dow Chemical). The determination of DEHP released was carried out also on a JASCO UV-vis apparatus at the corresponding  $\lambda_{max}$ . The amount of liquid entering the PVC was determined by weighing the PVC disk at the same time that the DEHP was measured. The transition temperature of the plasticized PVC was performed using a DSC 92 Setaram.

#### Chemicals

PVC is a commercial resin (Lucovyl, Rhone-Poulenc, Lyon, France) in the form of a white powder  $(M_n = 25,900 \text{ g mol}^{-1} \text{ and } M_w = 54,800 \text{ g mol}^{-1})$ . DEPH (Prolabo, Vaux en Velin, France), diethylhexyl adipate (Sigma, Saint-Quentin Fallavier, France), *n*-heptane (Fluka, Saint-Quentin Fallavier, France), isooctane (Fluka), absolute ethanol (SDS, Peypin, France), and absolute methanol (Sigma) were used as received.

### Preparation of the Plasticized PVC Samples

The plasticizer (DEHP) and PVC were mixed in methanol to obtain a homogeneous mixture. Then, methanol was completely evaporated at 60°C. The various compounds (PVC + DEHP) were pressed into sheets in a steel mold at 150°C and under a pressure of 100 bars. Discs of 13 (or

18) mm in diameter and 1 (or 3)-mm thick were cut from these PVC sheets.

# Preparation of the PVC Samples with Low Mass Tansfers

# First Stage

PVC disks were soaked in a liquid for a short period of time (e.g., 2 min). The liquid was n-heptane.

#### Second Stage

The disks were dried at various temperatures (20 and 100°C) and during various periods of time.

# Test for Determining the Rate of Plasticizer and Liquid Transfer

Diffusion experiments were conducted in a closed flask (50 cm<sup>3</sup>) and kept at 20  $\pm$  0.5°C or 30  $\pm$  0.5°C and at a controlled stirring rate. One PVC disk was immersed in 20 cm<sup>3</sup> of the liquid (*n*-heptane, arachid oil, isooctane, or ethanol).

At different times, the plasticizer was analyzed in the liquid and the disk was weighted to determine the liquid quantity entering the PVC. Experiments were repeated three times, and each experiment exhibited similar results because of the good homogeneity of the plasticized PVC sheets.

#### Theoretical

The curves (Fig. 1) that show the amount of DEHP released from treated PVC versus time are the same as those in the case of flow through a membrane,<sup>13</sup> when there is a uniform initial distribution and different surface concentrations.<sup>13</sup> Indeed, there is, first, a finite interval of time (the horizontal part of the curve) during which practically no transfer occurs; then, there is a straight line (whose the slope is equal to the flow of DEHP) that indicates that a steady state is reached.

To explain the transfers with treated PVC, one can suppose that new plastic is like a sandwich material: the original plasticized PVC between two sheets of PVC without a plasticizer (Fig. 2). Indeed, during the first stage (soaking of PVC in a liquid), two mass transfers take place, creating the formation of two steep gradients of concentration next to the plastic surface with a low concentration of DEHP and a high concentration of the liquid. After the second stage (evaporation of the liquid), one can consider that there is practically



**Figure 1** Amount of DEHP per unit area versus time. DEHP is released in different liquids from original plasticized PVC (at 35%, m/m) or treated plasticized PVC at 30°C (first soaking in *n*-heptane for 30 min and drying at the surrounding temperature): (a) arachid oil, thickness of the PVC disk: e = 3 mm; (b) *n*-heptane, thickness of the PVC dish: e = 3 mm; (c) ethanol, thickness of the PVC dish: e = 1 mm; (d) isooctane, thickness of the PVC disk: e = 1 mm.

no liquid near the PVC surfaces, and the treated PVC may be represented as the original PVC with two "membranes" of PVC without DEHP. The thickness of the "membrane" depends only on the loss of DEHP during the first stage.

#### Assumptions

With the PVC treated according to the process previously described, the fraction of DEHP lost



Figure 2 Diagram of the treated plasticized PVC.

may be simulated by adopting a time-lag method, on condition that we make the following assumptions:

- (i) The transfer is one-dimensionnal. The diffusion that occurs through the edges of the disk is negligible because the diameter is much larger than the thickness.
- (ii) The "membrane" is a very thin film practically without DEHP and without liquid. DEHP is lost during the first stage of the process while the liquid is evaporated during the second stage. The thickness of the membrane l is estimated according to the relationship

$$\frac{2l}{e} = \frac{m}{m_0} \tag{1}$$

m being the mass of DEHP released during the first stage;  $m_0$ , the initial amount in the disk; and e, the thickness of the disk. This valuation is justified by the steep gradient of DEHP near the surface at the beginning of the transfer.

- (iii) During the third stage, two simultaneous mass transfers take place: The liquid enters the PVC while the plasticizer leaves the polymer. These transfers involve three steps:
  - Diffusion in original PVC;
  - Diffusion in the "membrane;"
  - Crossing of the interface PVC-liquid and diffusion in the liquid.

Because the PVC of the "membrane" is in the glassy state (without a plasticizer, the  $T_{\sigma}$  of PVC is 357 K), the diffusion in the membrane is the slowest step. Indeed, the polymer in the glassy state has a very dense structure with very little internal void space. Glassy behavior is associated with chain stiffness and strong intermolecular forces between backbone chains. Hence, it is not surprising that penetrant diffusivities through such a structure are low. In contrast, polymers in the rubbery state like the original plasticizer PVC  $(T_{\rm g}$  = 262 K for 35%) are soft and flexible with such properties associated with freer chain motion. In this case, larger segments are thought to participate in the diffusion process and a larger amount of free volume in which diffusion may take place is more readily accessible. With the liquid stirred, one can suppose that the DEHP concentration does not depend on the space but only on the time. With the volume of the liquid being much larger than the disc, the concentration of DEHP in the liquid will be considered to be practically zero.

- (iiii) The amount of DEHP (or liquid) taken up by the membrane is a negligible fraction of the whole.
- (iiiii) The concentration profile of DEHP in the disk does not change during the second stage of the process.

#### Mathematical Treatment

The slowest step (crossing of DEHP or the liquid through the glassy polymer film) can be described by the basic equation for unsteady-state diffusion, called Fick's second law, in the case of a slab:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial_x^2} \quad 0 < x < l \tag{2}$$

*C* being the concentration of substance (the liquid or DEHP); *D*, the diffusivity in the membrane; *x*,

the space coordinate; and t, the time. The initial and boundary conditions are

For the plasticizer:

Cp being the concentration of DEHP at time t, and  $C_{p0}$ , the corresponding amount in the original PVC.  $t_d$  is the time during which no transfer occurs.

For the liquid:

 $C_L$  being the concentration of liquid in PVC, and  $C_{L,i}$  the corresponding amount at equilibrium.

The solutions of eq. (2) for the plasticizer and the boundary conditions were given by Crank<sup>13</sup>:

$$\frac{C_p}{C_{p_0}} = 1 - \frac{x}{l} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi x}{l}\right) \exp\left(-\frac{Dn^2 \pi^2 t}{l^2}\right)$$
(3)

If  $M_t$  denotes the amount of plasticizer which enters the membrane during time t, and  $M_{\infty}$ , the corresponding amount during infinite time, then

$$rac{M_t}{M_{\infty}} = 1 - rac{8}{\pi^2} \sum_{n=0}^{\infty} rac{1}{(2n+1)^2} \exp\!\left(-rac{D(2n+1)^2 \pi^2 t}{l^2}
ight)$$
(4)

The rate at which the plasticizer emerges from unit area of the face x = l of the film is given by

$$-D\left(\frac{\partial C_p}{\partial x}\right)_{x=l} \tag{5}$$

which is easily deduced from (3). Then, by integrating with respect to t, we obtain the total amount of DEHP,  $Q_t$ , which has passed through an unit area of the membrane in time t:

Liquid	$D_0 \; ({\rm cm}^2 \; {\rm s}^{-1})$	$D_1 \; ({\rm cm}^2 \; {\rm s}^{-1})$	$D_2 \; ({\rm cm}^2 \; {\rm s}^{-1})$
Arachid oil <i>n</i> -Heptane Ethanol Isooctane	$egin{array}{c} 2.1  imes 10^{-10} \ 7.0  imes 10^{-8} \ 1.2  imes 10^{-9} \ 3.8  imes 10^{-9} \end{array}$	$egin{array}{llllllllllllllllllllllllllllllllllll$	$5.2  imes 10^{-11} \ 2.0  imes \ 10^{-9} \ 7.9  imes 10^{-10} \ 1.2  imes \ 10^{-9}$

Table I Diffusivities of DEHP Estimated in Different Systems of PVC-Liquid

 $D_0$  is the diffusivity in PVC without treatment calculated with (8);  $D_1$ , the diffusivity calculated with (9); and  $D_2$ , the diffusivity calculated with (10).

$$Q_{t} = \frac{DC_{p}}{l} t - \frac{lC_{p}}{6} - \frac{2lC_{p}}{\pi^{2}} \sum_{n=1}^{\infty} \frac{(-1)^{n}}{n^{2}} \exp\left(-\frac{Dn^{2}\pi^{2}t}{l^{2}}\right)$$
(6)

For long times, the expression approaches the lines

$$Q_t = \frac{DC_p}{l} \left( t - \frac{l^2}{6D} \right) \tag{7}$$

A similar mathematical treatment gives the concentration  $C_L$  and the amount of liquid entering the membrane.

#### **Measurement of Diffusion Coefficients**

Quantitative measurements of the rate at which a diffusion process occurs are usually expressed in terms of a diffusivity. In this work, three diffusivities (for both the liquid and DEHP) are of interest during the whole transfer:

(i) The diffusion coefficient  $D_0$  during the first stage, that is, with the original PVC. It is calculated with the approximated equation valid for short times<sup>13</sup>:

$$\frac{n_t}{n_\infty} = 4 \left(\frac{D_0 t}{\pi e^2}\right)^{1/2} \tag{8}$$

where e is the thickness of the disk;  $m_t$ , the amount of plasticizer liberated (or liquid entering the disk) at time t, and  $m_{\infty}$ , the corresponding amount at equilibrium. In this case, we can consider that  $D_0$  is the diffusivity corresponding to the initial concentration of DEHP because this relationship is only valid for short times. (ii)The diffusivity  $D_1$  determined by the relationship of the time-lag method:

$$t_d = \frac{l^2}{6D_1} \tag{9}$$

In this case, the diffusion coefficient is an average value, because D varies with the concentration of the plasticizer and the liquid.<sup>14</sup> (iii) The last value of the diffusion coefficient  $D_2$  is given by the relationship deduced from the slope of the straight line of the curve:

$$p = \frac{D_2 C}{l} \tag{10}$$

where C is the mass of DEHP per volume unit in the original PVC, and l, the thickness of the membrane.

The value of D obtained during this steady state is the maximal value because the membrane is saturated.

Indeed, the plot of  $M_t/M_\infty$  calculated with (4) versus time (Fig. 5) indicates that the quantity of DEHP (or the liquid)  $M_t$  in the membrane is equal to  $M_\infty$  when the steady state is reached.

### **RESULTS AND DISCUSSION**

To prove that the assumptions and approximations are really conservative, calculated migration values according to the time-lag model were compared with the experimental migration data. The achieved experiences were chosen to show that the model can be employed with different operative conditions. Therefore, we tested the model with different soaking liquids in the third stage of the process, with different times of immersing during the first step, and by changing the initial concentration of the plasticizer in the original PVC.



**Figure 3** Influence of the time of immersion during the first stage of the process. The PVC is initially plasticized at 50% and e = 1 mm. (a) Amount of DEPH per unit area versus time. The PVC is first immersed in *n*-heptane for different times and dried at 100° for 5 min. PVC is soaked again in *n*-heptane at 20°C. (b) Time lag versus the square of membrane thickness.

# Influence of the Nature of the Liquid Used in the Third Stage

We selected the liquids from a practical point of view: Arachid oil is an aliment and *n*-heptane, isooctane, or ethanol are recommended by such bodies as the Food and Drug Administration or the Council of European Communities in order to simulate liquid foods.<sup>2–5</sup> In all the investigations presented in this subsection, the PVC is plasticized with 35% of DEHP, the temperature is 30°C, and the liquid used in the first stage of the process is *n*-heptane but other operative conditions are not the same as one can see in Figure 1.

The four curves indicate clearly that there is a reduction of mass transfer whatever the liquid used and that the curves have the same profile: A first part where there is no transfer, a linear part that indicates a steady state, while a last part that corresponds to equilibrium, that is, the whole DEHP has been released.

The time lag [therefore, the average diffusivity deduced from (9)] depends on the nature of the liquid. The decrease of the diffusion rate is greater with oil than with other liquids. But in all cases, the reduction of the release rate of DEHP is important as one can see in Table I and the

$l^2 (\mathrm{cm}^2)$	$t_d$ (s)	$D_0 \; ({ m cm}^2 \; { m s}^{-1})$	$D_1 \; ({ m cm}^2 \; { m s}^{-1})$	$D_2 \; ({\rm cm}^2 \; {\rm s}^{-1})$
$3.1~ imes~10^{-5}$	5,800	$3.3 imes10^{-7}$	$8.8 imes10^{-10}$	$12.0 imes10^{-9}$
$5.7~ imes~10^{-5}$	18,500	$3.3 imes10^{-7}$	$5.1 imes10^{-10}$	$9.4 imes10^{-9}$
$2.4~ imes~10^{-4}$	49,800	$3.3 imes10^{-7}$	$8.0 imes10^{-10}$	$2.9 imes10^{-9}$
$3.9~ imes~10^{-4}$	108,100	$3.3 imes10^{-7}$	$5.9 imes10^{-10}$	$2.8 imes10^{-9}$
$5.8~ imes~10^{-4}$	148,700	$3.3 imes10^{-7}$	$6.5 imes10^{-10}$	$4.7 imes10^{-9}$

Table II Diffusivities Calculated with the Model in the Case of PVC Plasticized at 50% and Treated by Soaking in *n*-Heptane for Different Times and Always Dried at 100°C for 5 Min

amount of DEHP liberated at equilibrium is much smaller than with the original PVC. For example, with arachid oil after 1200 h (or 50 days), only 2.5% of all the DEHP was liberated with treated PVC, instead of 11.5 with PVC without treatment.

# Influence of the Time of Immersing During the First Stage

The time of soaking during the first step of the process is an important factor because, according to our assumptions, it is responsible for the thickness of the membrane. Therefore, we studied the efficiency of the process by changing the time of immersion in the first step. We used a PVC plasticized with 50% of DEHP and *n*-heptane as the liquid. The temperature was 20°C and the soaking times were 2, 4, 16, 25, and 36 min.

Figure 3 shows that the time lag versus the square root of the membrane thickness is linear according to relationship (9). Therefore, these results indicate the validity of the model and show that the average diffusivity is practically the same as that in Table II. Indeed, the average of  $D_1$  values is about  $6.9 \times 10^{-10}$  cm<sup>2</sup> s<sup>-1</sup> and the value of D fluctuates from 6 to  $8.8 \times 10^{-10}$  cm<sup>2</sup> s<sup>-1</sup>.

#### Influence of Initial Concentration of Plasticizer

To study the influence of the initial concentration of DEHP on the decrease of mass transfer, we used two plasticized PVCs: one with 35% and another with 50% of DEHP. We selected the times of soaking during the first stage of the process so that the thickness of the membrane is the same in both cases.

Figure 4 shows that the reduction of the DEHP liberated is more important with the PVC plasticized at 35% of DEHP. Indeed, the diffusivity is smaller and the time lag is greater. We observe also in Figure 5(a) that liquid passes through the membrane faster than does DEHP. This confirms that the film is a PVC practically without DEHP and, therefore, a PVC in a glassy state. Then, the membrane is in a state with very little internal void space. Hence, it is not surprising that penetrant diffusivities through such a structure are low and that discrimination between diffusing substances on the basis of size is excellent. Therefore, it is normal that *n*-heptane diffuses faster than does DEHP, because the *n*-heptane molecule is smaller than the plasticizer. These results are in accord with recent works of Guo et al.<sup>14,15</sup>

# Validity of the Model

If we compare the experimental data (Figs. 4 and 5) with the calculated results, we can see a good correlation between them. In addition, we see that the time lag is proportional to the square root of the membrane thickness (i.e., the time of immersion in the first stage of the process) in accord with relationship (9). This fact demonstrates that the thickness of the membrane depends on the DEHP released during the first step of the process and that the evaluation of the thickness according to relationship (1) is valid.

At last, the diffusivities calculated with the model correlate well with those deduced from another investigation.<sup>16</sup> Indeed, their value depends on the DEHP and liquid concentration at a given time but also on the initial concentration of the plasticizer (Table III). The mean value calculated with (9) is always inferior to the value deduced from the slope of the linear part of the curve because the value obtained by this last method is the maximum value of the diffusion coefficient. Indeed, during the steady state, the membrane is saturated, that is, in the case of the treated PVC, the concentration of the liquid and of DEHP is maximum. This fact is corroborated by the determination of the amount of both diffusing substances absorbed at time  $t_s$  ( $t_s$  being the time at



**Figure 4** Influence of the initial concentration of the plasticizer. The thickness of the membrance evaluated from relationship (9) is about the same  $(l = 7.10^{-3} \text{ cm})$  in both cases. Temperature is 20°C and e = 1 mm. (a) Amount of DEPH released from PVC initially plasticized at 35% and PVC treated by soaking 7 min in *n*-heptane, dried at 100°C for 5 min. (b) Amount of DEHP released from PVC initially plasticized at 50% and PVC treated by soaking 4 min in *n*-heptane, dried at 100°C for 5 min.

which the steady state is reached), according to relation (4). The curve (Fig. 5) that represents  $M_t/M_{\infty}$  versus time shows effectively that the membrane is saturated when the steady state is reached.

# **CONCLUSIONS**

From this work, it can be concluded that the timelag model allows one to simulate the mass transfers between liquid and a treated plasticized PVC according to the process previously described. Indeed, the calculated values correspond correctly with the experimental data.

The diffusivities deduced from this model permit one to quantify the influence of parameters that play a role in this decrease of mass transfers. Therefore, this model may be useful to optimize the process. As a result, it is possible to prepare any packaging plasticized PVC without mass transfers at least during some time. The optimal



**Figure 5** Amount of DEHP and amount of *n*-heptane absorbed by the membrance during the third stage of the process at 20° C. PVC is initially plasticized at 35%. It is treated by soaking 150 s in *n*-heptane absorbed by the PVC disk. (b) Amount of DEHP and *n*-heptane absorbed only by the membrane.  $M_t/M_{\infty}$  is calculated by relationship (4).  $t_s$  is the time at which the steady state is reached.

efficiency of PVC packaging may be reached when the characteristics of the process are previously programmed. From a theoretical point of view,

Table III	Influence of	f the	Initial	Concentrati	on
of DEHP	on Diffusivit	ies			

Original % of DEHP	$D_0 \ ({ m cm}^2 { m s}^{-1})$	$D_{1} \ ({ m cm}^{2} { m s}^{-1})$	$D_2 \ ({ m cm}^2 { m s}^{-1})$
35 50	$6.0 imes 10^{-8}\ 3.3 imes 10^{-7}$	$\begin{array}{c} 4.9\times 10^{-11} \\ 5.1\times 10^{-10} \end{array}$	$rac{1.0 imes 10^{-9}}{9.4 imes 10^{-9}}$

Diffusivities calculated with the model in system PVC at 35% (or 50%) treated or not treated. Liquid: *n*-heptane.

this work contributes to a better understanding of the reduction of mass transfers and a deeper understanding will lead to consolidating the framework required for the attainment of a unified picture of diffusion in and through polymers.

# REFERENCES

- 1. Haesen, G.; Schwarze, A. In Migration Phenomena in Food Packaging; Commission of the European Communities: Office for Official Publications of the European Communities, 1978.
- Council of Europen Communities; Off J Eur Commun 1982, Oct. 23.

- 3. Council of Europen Communities;Off J Eur Commun 1985, Dec. 31.
- 4. Food and Drug Administration. Recommendations for Chemistry Data for Indirect Good Additives Petitions; Food and Drug Administration. Department of Health and Human Services: Washington, DC, 1988.
- 5. FDA Guidelines for Chemistry and Technology Requirements of Indirect Food Additive Petitions; Division of Food Chemistry and Technology. Center for Food Safety and Applied Nutrition, Food and Drug Administration. Department of Health and Human Services: Washington, DC, 1976.
- 6. Taverdet, J. L. Thesis, University of Saint-Etienne, France, June 1985.
- Feigenbaum, A. E.; Ducruet, V. J.; Delpal, S.; Wolff, N.; Gabel, J. P.; and Wittman, J. C. J Agr Food Chem 1991, 39.

- Taverdet, J. L.; Vergnaud, J. M. J Appl Polym Sci 1984, 29, 3391.
- Taverdet, J. L.; Vergnaud, J. M. Eur Polym J 1986, 22, 959.
- Senoune, A.; Vergnaud, J. M. Eur Polym J 1992, 28, 311.
- Senoune, A. Thesis, University of Saint-Etienne, France, Mar. 1993.
- Khatir, Y.; Taverdet, J. L.; Vergnaud, J. M. J Polym Eng 1989, 8, 111.
- Crank, J. In The Mathematics of Diffusion, 2nd ed.; Oxford University Press: Oxford, 1975.
- 14. Guo, C. J.; De Kee, D. Chem Eng Sci 1991, 46, 2141.
- Guo, C. J.; De Kee, D.; Harrison, B. Chem Eng Sci 1992, 47, 1525–1532.
- Taverdet, J. L.; Vergnaud, J. M. J Appl Polym Sci 1986, 31, 111. (5)