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Kinetic behaviour of chemical reactions in homogeneous and heterogeneous polymer melts

Guo-Hua Hu*, Sébastien Triouleyre and Morand Lambla
Laboratoire d'Extrusion Réactive, ECPM - Département Polymères, 4, rue Boussingault, 67000 Strasbourg, France
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This paper compares the kinetic behaviour of a given chemical reaction in homogeneous and heterogeneous polymer melts using a batch mixer as reactor. The underlying chemistry was the addition esterification of epoxy groups attached to a polymer backbone and a carboxylic acid. Specifically, the homogeneous polymer melt was composed of 1-naphthylacetic acid (NAA) and a random copolymer of ethylene, ethyl acrylate and glycidyl methacrylate (CoGMA). The organic acid was soluble in the CoGMA melt under the reaction conditions. The heterogeneous polymer melt was the aforementioned homogeneous polymer melt to which was added an inert polymer, polystyrene (PS). The PS and the CoGMA were immiscible while NAA was miscible with both polymers. Experimental results showed that the overall reaction rate in the homogeneous polymer melt was controlled by its intrinsic kinetics only while that in the heterogeneous polymer melt was dictated not only by the intrinsic kinetics, which is the same as that in the homogeneous polymer melt, but also by the partition coefficient of NAA between the CoGMA and the PS phases. These results can be justified by the fact that the rate of diffusion of NAA is much greater than the rate of reaction for both homogeneous and heterogeneous polymer melt systems, as mechanical mixing was necessary only at the initial stage of the reaction. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: chemical reaction; kinetics; partition coefficient; diffusion; polymer melt)

INTRODUCTION

It has been common practice to run chemical reactions involving polymers in the presence of a liquid carrier. Due to the ever-growing concerns about the environmental impact of the excessive use of solvents, reactions have been run more and more in solventless polymer melts[1]. In the absence of solvents, the reaction pathway would be complicated by numerous factors such as heterogeneity of the reacting mixture and slow diffusion of reactants[2]. A fundamental question arises of whether a chemical reaction carried out in a melt behaves differently from the same reaction in solution, and to what extent they differ.

For a particular chemical reaction, its overall rate depends, among other things, on how the various reacting species involved are mixed. In the absence of solvents, the reacting system can be homogeneous, heterogeneous or something in between. When a chemical reaction is to be carried out in a molten polymer medium without any solvents, the simplest case is that the reacting system is homogeneous. This situation was examined previously with model reacting systems composed of a polymer bearing a certain number of functional groups along its backbone and a small reactive molecule[3,4]. Comparison of the kinetic results generated in solution with those in the homogeneous polymer melt led to the conclusion that if the characteristic diffusion time of the small reactive molecule is much greater than the characteristic time of the reaction, then the reaction mechanism and the intrinsic reaction constants will be expected to be identical in both media provided that the solvent does not interfere with the reaction in any way. In this case, the sole difference lies in that the overall reaction rate in the melt is much greater because of greater concentrations of the reacting species.

The main objective of this study was to compare the kinetic behaviour of a given chemical reaction carried out in homogeneous and heterogeneous polymer melts. The underlying chemistry chosen was the addition esterification between an epoxy group and a carboxylic group. Specifically, the homogeneous reacting system was composed of 1-naphthylacetic acid (NAA) and a copolymer of ethylene, ethyl acrylate and glycidyl methacrylate (CoGMA). The heterogeneous reacting system was the above-mentioned homogeneous reacting system to which was added an inert polymer, polystyrene (PS). The PS and CoGMA were immiscible while NAA was miscible with both polymer melts in the range of chemical compositions and temperatures covered in this study.

EXPERIMENTAL

Materials

The polymer bearing epoxy groups was a random copolymer (CoGMA). It was kindly supplied by

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* To whom correspondence should be addressed

Atochem, France. The three monomer units involved in the copolymer (ethylene, ethyl acrylate and glycidyl methacrylate) weighed 68.0, 24.0 and 8.0 wt%, respectively. Its number-average and weight-average molecular weights were 10 000 and 31 000 g mol^{-1}, respectively. The melting temperature of this copolymer ranged from about 36 to 86°C. NAA (melting point: ~130°C) was purchased from Aldrich and used as received. PS from Atochem was used as the inert polymer. Its number-average and weight-average molecular weights were 175 000 and 400 000 gmol^{-1}, respectively. The solubility of NAA in the PS was about 25 wt% at 50°C, and greater in CoGMA.

Reaction procedures

A batch mixer of the Rheocord Haake type was used as the reactor because a beaker, a kettle or a stirred autoclave, used largely by chemists or chemical engineers as reactors, was not suitable in this study due to its inability to mix viscous fluids. The chamber of this batch mixer (50 cm^3) consisted of three separate metallic plates. The temperature of each plate was controlled by a temperature controller. The temperature of the reacting system was followed up by a thermocouple which was in contact with it. Two sigma rotors were placed in the chamber to ensure mixing.

For a typical experiment run, the reacting system was composed of CoGMA (46.0 g) and NAA (4.0 g), corresponding to 8.0 wt% of NAA. They were premixed in a cup before being added to the chamber of the mixer. This latter was preheated up to a desired temperature (140, 150, 160 or 170°C). The temperature of the reactive mixture was controlled within ± 1.5°C. The rotation speed of the rotors was 64 rev min^{-1}., unless specified otherwise. For the reaction runs where the PS was added, the total amount of the CoGMA and PS was kept at 47.5 g while that of NAA was 2.5 g, corresponding to 5.0 wt% of NAA. Samples were taken at various chosen times (between 5 and 90 min) and quenched in liquid nitrogen to prevent further reactions.

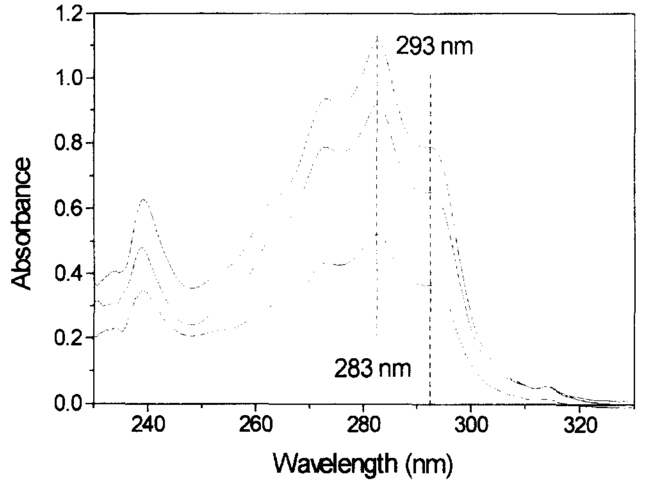


Figure 1 U.v. spectra of three NAA modified CoGMA samples in

Conversion measurement

Samples collected from the batch mixer were purified by dissolving in xylene, precipitation in methanol, redissolving in chloroform and reprecipitation in methanol. They were then dried at 50°C in a vacuum overnight. The conversions of those samples were measured using a u.v. spectrophotometer in chloroform. Shown in *Figure 1* are the u.v. spectra of three NAA modified CoGMA samples. In this study, the peak at 293 nm was used to calculate the conversions with a pre-established calibration curve. The reason for using the peak at 293 nm instead of the one at 283 nm as the target was that when PS was used as an inert polymer, its u.v. absorption curve overlapped more or less with the peak at 283 nm.

RESULTS AND DISCUSSION

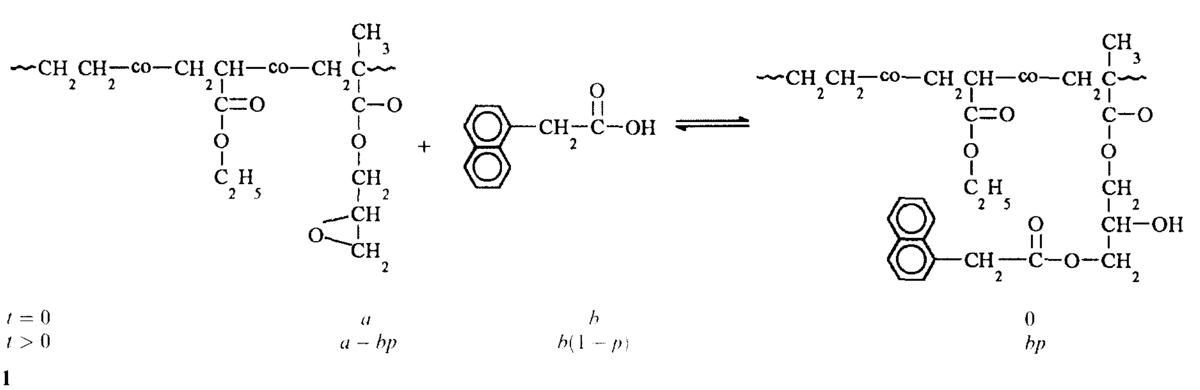
The underlying chemistry between the epoxy group of the epoxy-bearing random copolymer (CoGMA) and NAA can be represented by *Scheme 1*, where a and b are the initial molar concentrations of the epoxy group of CoGMA and that of the acid, respectively, and p denotes the conversion with regard to the acid consumption. The reaction scheme ignores the reactivity of the secondary hydroxyl group towards the epoxy group, which can be justified[5,6].

Similar to the addition esterification between an anhydride group and a hydroxyl group[7], the addition esterification between an epoxy group and a carboxylic group can be considered as being reversible, with the forward reaction being of first order with respect to the epoxy group and the acid group, and the reverse reaction being of first order with respect to the newly formed group. Accordingly, the overall conversion rate can be described by

$$\frac{dp}{dt} = k_1(a - bp)(1 - p) - k_2 p \qquad (1)$$

where k_1 and k_2 are the forward and reverse reaction constants. Integration of equation (1) yields

$$\frac{1}{\Delta}\ln\frac{(2bp + \alpha - \Delta)(\alpha + \Delta)}{(2bp + \alpha + \Delta)(\alpha - \Delta)} = k_1 t \qquad (2)$$



Scheme 1

where $\alpha = -(a + b + 1/K_e)$, K_e is the equilibrium constant and $\Delta = \sqrt{\alpha^2 - 4ab}$.

The constants k_1 and k_2 under given reaction conditions can be obtained by a minimization process with the following objective function:

$$S(k_1, k_2) = Min \sum_{i=1}^{N} \left(\frac{1}{\Delta} \ln \frac{(2bp_i + \alpha - \Delta)(\alpha + \Delta)}{(2bp_i + \alpha + \Delta)(\alpha - \Delta)} - k_1 t_i \right)^2 \quad (3)$$

This objective function contains two targeted variables: k_1 and k_2. The equilibrium constant K_e can be calculated from the ratio of k_1/k_2, or determined from the equilibrium conversion p_e:

$$K_e = \frac{k_1}{k_2} = \frac{p_e}{(a - bp_e)(1 - p_e)} \quad (4)$$

Equations (1) and (4) are the governing equations for the homogeneous reacting system composed of NAA + CoGMA if the overall reaction is not diffusion controlled.

In the case of the heterogeneous reacting system composed of NAA + CoGMA + PS, the small reactive molecule NAA is partitioned between both the CoGMA and PS phases. If the molecular diffusion rate of the acid in these two polymeric phases is so rapid that a partition equilibrium is always established between them in terms of the acid concentration, and the overall reaction rate is not controlled by the diffusion of the acid, then the conversion rate is expected to be given by

$$\frac{dp}{dt} = k_1' \left(\frac{n_1}{v_1 + v_i/\epsilon} - \frac{n_2 p}{v_1 + v_i/\epsilon} \right)(1 - p) - k_2' p$$
$$= k_1'(A - Bp)(1 - p) - k_2' p \quad (1')$$

when n_1 and n_2 denote the molar numbers of epoxy groups in CoGMA and in the acid, respectively; v_1 and v_i are the volumes of the CoGMA phase and of the PS phase, respectively; ϵ is the partition coefficient of the acid, which is defined as the ratio of its amount in the CoGMA phase over that in the PS phase; $A = n_1/(v_1 + v_i/\epsilon)$ and $B = n_2/(v_1 + v_i/\epsilon)$. A and B can be called the apparent initial molar concentrations of the epoxy group in CoGMA and in the acid, respectively.

Integration of equation (1′) yields

$$\frac{1}{\Delta'} \ln \frac{(2Bp + \alpha' - \Delta')(\alpha' + \Delta')}{(2Bp + \alpha' + \Delta')(\alpha' - \Delta')} = k_1' t \quad (2')$$

where $\alpha' = -(A + B + 1/K_e')$, K_e' is the equilibrium constant and $\Delta' = \sqrt{\alpha'^2 - 4AB}$.

Similar to the homogeneous reacting system, the constants k_1' and k_2' in equation (1′) can also be obtained by a minimization process with the following objective function:

$$S(k_1', k_2', \epsilon) = Min \sum_{i=1}^{N} \left(\frac{1}{\Delta} \ln \frac{(2Bp_i + \alpha' - \Delta')(\alpha' + \Delta')}{(2Bp_i + \alpha' + \Delta')(\alpha' - \Delta')} - k_1' t_i \right)^2 \quad (3')$$

Compared to equation (3) for the homogeneous reacting system, this objective function contains one additional targeted variable: the partition coefficient ϵ.

The equilibrium constant K_e' of this heterogeneous reacting system can be calculated from the ratio of k_1'/k_2', or determined from the equilibrium conversion p_e':

$$K_e' = \frac{k_1'}{k_2'} = \frac{p_e'}{(A - Bp_e')(1 - p_e')} \quad (4')$$

Equations (1′) and (4′) are the governing equations for the kinetics of this heterogeneous reacting system under the above-mentioned assumptions. Note that when ϵ is infinite, or NAA is completely immiscible with the chemically inert PS phase and is solubilized only in the CoGMA phase, then equations (1′)–(4′) will reduce to equations (1)–(4), respectively; on the other hand, when ϵ is zero, or NAA is completely immiscible with the reactive copolymer CoGMA and is solubilized only in the chemically inert PS phase, then no reaction will occur.

Inspection of equations (1)–(4) and equations (1′)–(4′) indicates that when ϵ is not infinite or zero, the main difference between the homogeneous and the heterogeneous reacting systems lies in that, in this latter case, the overall reaction rate is controlled not only by its intrinsic kinetics but by the partition coefficient of the acid as well. This partition coefficient is determined by the thermodynamic properties of the two polymers of interest. Below we will examine the kinetic behaviour of these two reacting systems.

Before doing so, the reversibility of the above-mentioned reaction was checked. This was done by heating an NAA-esterified CoGMA sample free of NAA at 160°C for about 30 min. It was found that the reverse reaction, formation of NAA and CoGMA from the NAA-esterified CoGMA, did take place under these conditions, but side-reactions also occurred that interfered with the attainment of the expected equilibrium. This would affect the values of the reaction rate constants and the equilibrium constant derived from the above-described methods. However, since the side-reactions should be of minor importance at relatively low concentrations of NAA, it is believed that the values derived should not require substantial correction. The main conclusions of the paper remain unaffected.

Kinetics in the homogeneous reacting system

The conversion as a function of mixing time for the CoGMA + NAA homogeneous reacting system is shown in *Figure 2* for four different temperatures. Note that at a particular temperature the acid conversion tends to level off, indicating that this reaction is reversible. Moreover, the equilibrium favours the formation of the product when raising the temperature. The solid curves in this figure are generated from equation (2) upon inserting the values of the forward and reverse rate constants, k_1 and k_2. The latter are obtained from the minimization process according to equation (3) using the NAA conversion data points, which are some 80% lower than the respective plateau values. The relatively good agreement between the experimental data points and the calculated solid curves supports the proposed overall reaction mechanism. It also suggests that the overall reaction is not diffusion controlled.

The applicability of equation (2) to the homogeneous reacting system of CoGMA + NAA is further corroborated by *Figure 3*, in which is plotted the conversion of NAA as a function of time at 140°C for three different

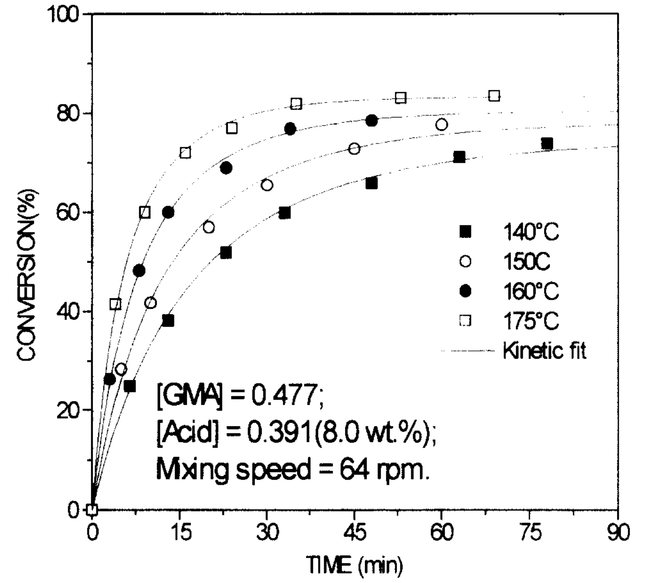


Figure 2 Conversion as a function of time for the reaction between CoGMA and NAA in the homogeneous melt at four different temperatures. The solid curves are the results calculated from equation (2)

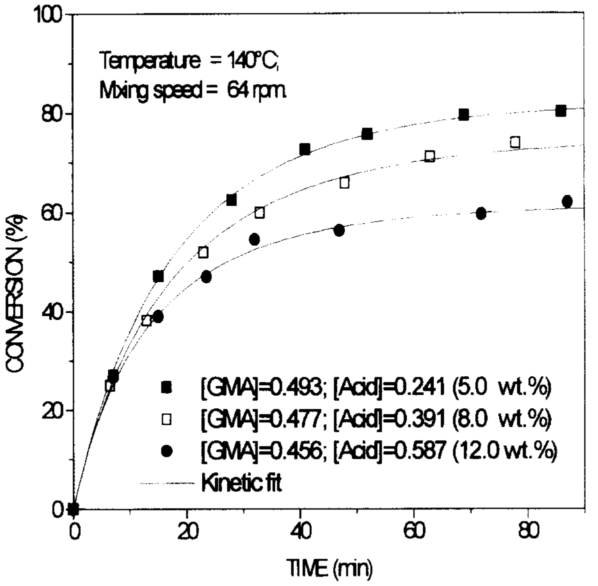


Figure 3 Conversion as a function of time for the reaction between CoGMA and NAA in the homogeneous melt at 140°C for three different initial NAA concentrations. The solid curves are the results calculated from equation (2)

Table 1 Kinetic constants (k_1, k_2 and K_e) obtained at three different initial NAA concentrations

CoGMA (wt%)	NAA (wt%)	k_1 (M min)$^{-1}$	k_2 (min)$^{-1}$	K_e (λ)M^{-1}
95.0	5.0	0.10	0.0068	15.3
92.0	8.0	0.11	0.0065	16.1
88.0	12.0	0.11	0.0071	16.1

initial NAA concentrations. Here again, the back-calculated solid curves match fairly well the experimental data points. Also, the k_1 and k_2 values are, within experimental error, independent of the initial NAA concentration (*Table 1*). This also suggests that the possible autocatalysis of the acid (NAA) in this melt reaction between the epoxy group of CoGMA and NAA should be very weak.

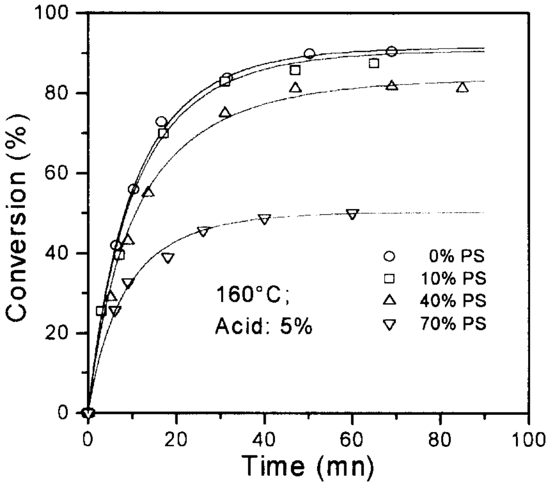


Figure 4 Conversion as a function of time of the heterogeneous reacting system of CoGMA + PA + NAA at 160°C for four different proportions of PS: 0, 10, 40 and 70 wt% (temperature = 160°C; rotating speed, 64 rev min^{-1})

Kinetic behaviour in the heterogeneous reacting system

The conversion as a function of mixing time for the PS + CoGMA + NAA heterogeneous reacting system at 160°C is shown in *Figure 4* for four different PS proportions: 0, 10, 40 and 70 wt%. Similar to what is seen for the CoGMA + NAA homogeneous reacting system, the acid conversion in the heterogeneous reacting system levels off with time for a particular PS fraction. Also, the conversion rate and equilibrium conversion decrease with increasing PS fraction, due, at least in part, to a reduced NAA concentration in the CoGMA phase.

The solid curves in *Figure 4* are generated from equation (2′) using the values of the forward and reverse rate constants, k_1' and k_2'. The latter are determined as follows: insert into equation (3′) all the experimental conversion data obtained at the various PS weight fractions which correspond to 80% of the respective plateau values, and then search for the minimum for $S(k_1', k_2', \epsilon)$. Because the partition coefficient ϵ is unknown experimentally, it is also a targeted variable in equation (3′). Obviously, this minimization process makes sense only when the values of k_1' and k_2' obtained allow equation (2′) to generate conversion values that agree with all the experimental data obtained with the various PS weight fractions. Additionally, the value of ϵ should be reasonable. Indeed, the calculated conversions (solid curves in *Figure 4*) agree reasonably well with the experimental data. This agreement also indicates that the reaction between CoGMA and the acid in this heterogeneous reacting system is not diffusion controlled: it follows the same reaction mechanism as that in the homogeneous reacting system composed of CoGMA and NAA. On the other hand, the ϵ-value is found to be 6.9, meaning that the amount of acid in the CoGMA phase is 6.9 times that in the PS phase. This may be due to a much lower number molecular weight of the CoGMA (10 000 g mol^{-1}) than that of the PS (175 000 g mol^{-1}). Also the interaction between the polar groups of CoGMA (ethyl acrylate and glycidyl methacrylate) and the carboxylic group of NAA may dominate that between the styrenic moiety of the PS and the naphthyl group of NAA.

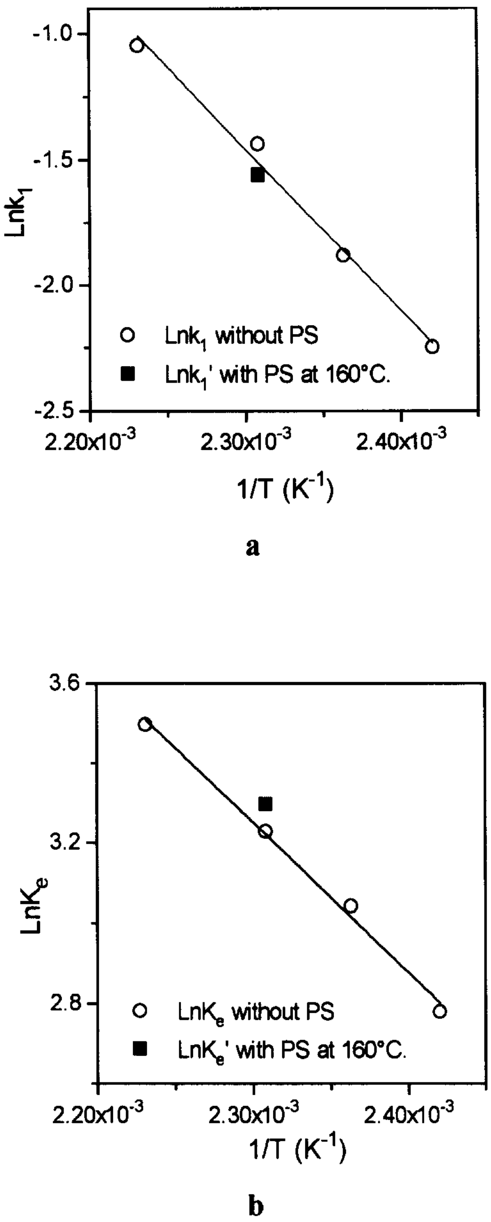


Figure 5 Kinetic comparison between the homogeneous and heterogeneous reacting systems. (a) Temperature dependence of the forward reaction rate constant with $k_1 = 6.68 \times 10^5 e^{-6464/T}$ (M min)$^{-1}$; (b) temperature dependence of the equilibrium constant with $K_e = 1.44 \times 10^5 e^{-3749/T}$

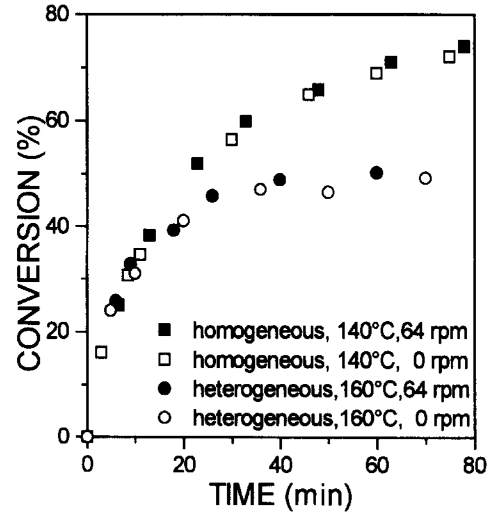


Figure 6 Mechanical mixing effect on the overall rate of the reaction in the homogeneous reacting system (CoGMA + NAA) and in the heterogeneous reacting system (PS + CoGMA + NAA)

Kinetic comparison between the homogeneous and heterogeneous reacting systems

It has been shown above that the reaction carried out in the homogeneous reacting system (CoGMA + NAA) and in the heterogeneous reacting system (PS+ CoGMA + NAA) is not diffusion controlled. Furthermore, the reaction mechanism of the heterogeneous reacting system is identical to that in the homogeneous one. The only fundamental difference is that in the former, the overall reaction rate is controlled by an additional parameter: the partition coefficient of the acid between the reactive polymer (CoGMA) and the inert one (PS). Accordingly, this parameter should be taken into account in the kinetic analysis.

One may wonder if the above statements are valid; the values of the forward rate constant (k_1') and the equilibrium constant (K_e') in the heterogeneous reacting system should be the same as those of the homogeneous one at the same temperature, say, 160°C, regardless of the PS proportion. This is indeed true, as shown in *Figures 5a* and *5b*.

Effect of mechanical mixing on the overall reaction rate

In order to further support the above argument that diffusion of the acid in the homogeneous and heterogeneous systems is so rapid that it is not the rate-limiting step, the effect of mechanical mixing was examined. Specifically, the reaction in the homogeneous reacting system containing 8.0 wt% NAA was run either with the rotors of the mixer rotating at 64 rev min^{-1} for the entire reaction time; or at 64 rev min^{-1} for the first 3 min only and thereafter no more mechanical mixing. The heterogeneous reacting system containing 70 wt% of PS and 5.0 wt% of NAA was also run in the mixer in a similar manner. For both reacting systems, the conversion–time curves obtained under the above-mentioned two different mixing modes match fairly well, as shown in *Figure 6*. This indicates that the diffusion rate of NAA is indeed much greater than the rate of reaction. Otherwise, mechanical mixing should have affected the overall reaction rate.

The fact that 3 min of mixing at 64 rev min^{-1} is already long enough to homogenize both reacting systems can be sustained upon comparing the characteristic reaction time, t_R, with the characteristic molecular diffusion time of NAA, t_D. The former is of the order of $1/k_1a$ or 15 min while the latter can be expressed by h^2/D. If h, the characteristic diffusion length, is taken as 1×10^{-5} m and D, the diffusion coefficient of NAA, as 1×10^{-10} m^{2}s^{-1}, then t_D is of the order of seconds, which is much shorter than t_R. This indicates that the role of mechanical mixing is to help disperse the acid in CoGMA or in the mixing of CoGMA + PS, and to reduce the diffusion length to a sufficiently small scale.

CONCLUSIONS

This paper has attempted to compare the kinetic behaviour of chemical reactions involving polymers in a homogeneous melt (in the absence of solvents) with that in a heterogeneous melt using a batch mixer as a reactor. The underlying chemistry chosen has been based on the reactivity between an epoxy group and a carboxylic group. More specifically, the homogeneous reacting system is a mixture of NAA and a random copolymer (CoGMA). The heterogeneous reacting system is the above homogeneous reacting system to which is added an inert polymer, polystyrene (PS). The PS and CoGMA are immiscible while NAA is miscible with both polymers. Experimental results have shown that the overall rate of the homogeneous reacting system is controlled by its intrinsic kinetics only while that of the heterogeneous reacting system is dictated not only by its intrinsic kinetics, which is the same as that of the homogeneous reacting system, but also by the partition coefficient of NAA between the CoGMA and PS phases. These results are supported by the fact that the overall rate of reaction is much lower than the rate of diffusion of the acid, which is consistent with the observation that mechanical mixing is necessary only at the initial stage of the reaction (less than 3 min).

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