Transesterification Reaction of Poly(Ethylene-co-Vinyl Acetate) with Alcohols: A Kinetic Study in Solution and in the Bulk

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SYNOPSIS

The chemical kinetics of the transesterification reaction of poly(ethylene-co-vinyl acetate) (EVA) with aliphatic alcohols were investigated, both in solution and in bulk, in the presence of dibutyl tin dilaurate (DBTDL) as the catalyst. A Fourier Transform infrared spectrometer (FTIR) was utilized for the measurement of the extent of the reaction. Experimental results showed that the reaction carried out in solution and in the bulk follows the same mechanism, namely, a reversible second order reaction of which the equilibrium only slightly increases with temperature. Additionally, the overall forward and reverse rate constants are proportional to the square root of the concentration of the catalyst. This study has also revealed that the intrinsic rate constants in solution and in the bulk are the same, regardless of the differences in the physical conditions encountered in the bulk and solution media, in particular, the reactant concentrations and viscosity of the reacting mixture. The effects of mechanical mixing are unimportant, since the reaction rate is relatively slow as compared with the rate of diffusion.

INTRODUCTION

Traditionally, both the chemistry and the engineering practice involving reacting polymer systems have utilized inert carrier liquids to avoid complications caused by the high viscosity of undiluted bulk systems. Deficient mixing, poor temperature control, slow diffusion of reactants, and by-products can contribute to the apparent transport limitations associated with high viscosity. From a chemical vantage point, the presence of a proper solvent can favorably affect the selectivity and the rate of reaction.

On the other hand, reactive processing in general, and reactive extrusion in particular, tends to eliminate the use of solvents for both economic and environmental reasons. The use of chemical reactions under the above mentioned, ill-defined conditions typical of bulk media, obscures the understanding of the process at both the chemical and transport levels. The understanding of reaction mechanisms used in molten state reactive extrusion is poor, in general.

In this article, a comparison is given between the reaction kinetics of a transesterification reaction between poly(ethylene-co-vinyl acetate) and aliphatic alcohols in the respective presence and absence of solvent. The purpose of this study is twofold:

1. To examine possible mechanistic effects of the two reaction environments for this class of chemical reactions and
2. To rationalize kinetics characterization measurements for such reactions, required by, for example, reactive processing analysis.

EXPERIMENTAL

Materials

The polymer substrate used as a reactant in the transesterification reaction was a commercial

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(ATOCHEM) grade of ethylene–vinyl acetate random copolymer with a 14% vinyl acetate content (Mn = 21,000 g/mol, Mw/Mn = 3.5).

1-Octanol, 2-ethyl 1-hexanol, and 3-phenyl 1-propanol were used as the alternative reactants. The reactions were catalyzed by dibutyl tin dilaurate (DBTL). 1-Dodecane was used as the solvent.

Some selected data concerning the alcohols and the solvent are shown in Table I.

Procedures

The reaction in solution was conducted in a stirred, three neck flask (0.5 l), equipped with a single glass blade, rotating at 150 rpm. The reaction temperature was controlled by a silicon oil bath within 0.5°C.
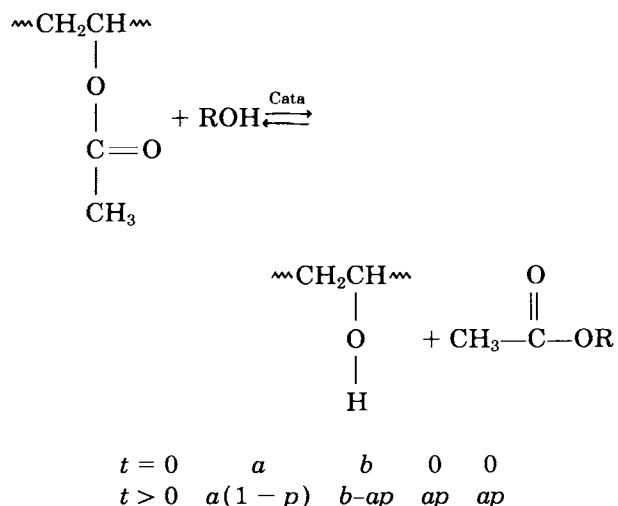
The bulk reaction was carried out in a Rheocord Haake mixer (50 cm³). There were two counter-rotating sigma rotors in the mixing chamber running at 64 rpm. The reaction temperature was controlled by a temperature controller.

In both cases, samples were collected, precipitated in acetone, filtered, redissolved in 1-octane, and re-precipitated in acetone. Finally, the polymer samples were dried at 80°C under vacuum overnight for analysis.

A Fourier transformed infrared spectrometer was used to determine the conversion of the reaction.[1,2]

RESULTS AND DISCUSSION

The vinyl acetate group in the poly(ethylene-co-vinyl acetate) can be converted into the corresponding vinyl alcohol group by reaction with an alcohol.[2,3] This transesterification reaction can be represented as follows:

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∿CH₂CH∿
   |
   O
   |        Cata
   |  + ROH ⇌
  C=O
   |
  CH₃
```

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      ∿CH₂CH∿            O
         |               ||
         O     + CH₃—C—OR
         |
         H
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$t = 0$ a b 0   0
$t > 0$ $a(1-p)$ $b-ap$ ap ap

Table I Physical Properties of Alcohols

	F.W. (g/mol)	M.P. (°C)	B.P. (°C)
1-octanol	130.23	−15	196
2-ethyl 1-hexanol	130.23	−76	184
3-phenyl 1-propanol	136.19	−18	235

Note: These alcohols were purchased from Aldrich Company. The data indicated are those quoted in the catalogue.

where a and b denote the initial molar concentration of the vinyl acetate group and the alcohol, respectively and p is the conversion in terms to the vinyl acetate group concentration.

It has been shown that this is a reversible reaction, both the forward and reverse reactions being of second order.[2] If their rate constants are denoted as k_1 and k_2, the overall reaction rate can be written as:

$$V = -\frac{d(a - ap)}{dt}$$
$$= k_1(a - ap)(b - ap) - k_2(ap)(ap) \quad (1)$$

Upon introduction of the functional ratio, $r = b/a$, the above equation becomes:

$$\frac{dp}{dt} = k_1 a(1 - p)(r - p) - k_2 a p^2 \quad (2)$$

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

$$K_e = \frac{k_1}{k_2} = \frac{p_e^2}{(1 - p_e)(r - p_e)} \quad (3)$$

Equations (2) and (3) are the governing equations for this reaction, wherein the rate constants k_1 and k_2, (and equilibrium constant K_e) are to be determined experimentally.

Reactivity of Different Alcohols

Figure 1 shows the conversion as a function of time for the reaction carried out in solution of 1-dodecane at 152.5°C for 1-octanol and 3-phenyl 1-propanol, respectively. The results show that, for the two very
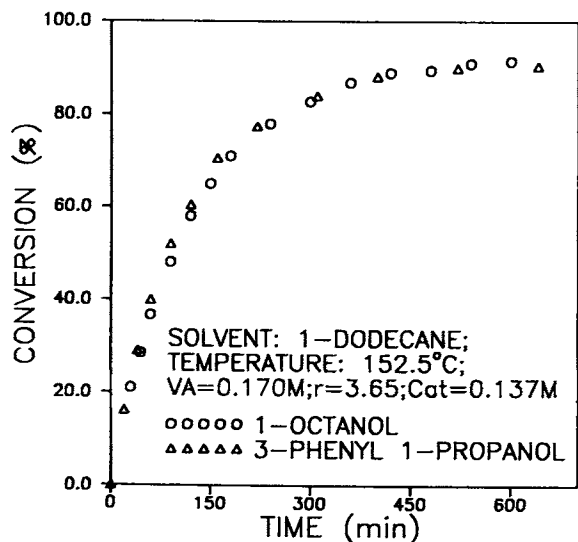
Figure 1   Reactivity of different alcohols in solution.

Figure 2   Reactivity of different alcohols in the bulk.

different alcohols used, no difference in the course of the chemical reaction has been found.*

Figure 2 presents the situation for bulk transesterification, using, in addition to these two alcohols, 2-ethyl 1-hexanol. Also, when these three different alcohols are used, no difference in reactivity was seen at any given temperature.

These results imply that when studying the kinetics of the transesterification reaction, the use of any one of these alcohols is sufficient.

Reaction Order in Solution and in the Bulk

For studies of the kinetics of transesterification in a more systematic fashion, 3-phenyl 1-propanol (PPOH) has been chosen; the phenyl group being an easy target for spectroscopic analysis of chemical conversion.

Figures 3 and 4 show parametric lines of the conversion as a function of time in solution and in the bulk, respectively, at various temperatures. The results demonstrate that this is an equilibrium reaction, for which the equilibrium constant is only slightly temperature dependent.

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* Adkins et al. compared the reactivity of a series of alcohols towards a given acetate in terms of their equilibrium constants.[4,5] The overall reaction was: R-OH + $CH_3CH_2OOCCH_3 \leftrightarrow CH_3CH_2$-OR + CH_3OH. They found that the equilibrium constant of this particular reaction at 200°C was 0.72, 1.02, and 0.69 for 1-octanol, 2-ethyl 1-hexanol, and 3-phenyl 1-propanol, respectively. It is interesting to note that the equilibrium constants for these alcohols are practically the same in the case of polymeric reacting systems, and they are also much higher (4.1 at 150°C and 4.6 at 180°C).
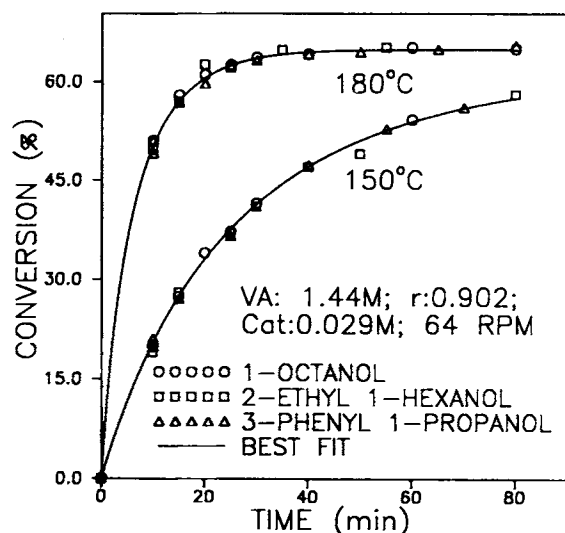
The reaction proceeds much more slowly in solution, even though the alcohol in this case is in a large excess ($r = 3.65$). In order to obtain the rate constants of this reaction rate in these two different reacting media, eq. (2) was utilized to fit the data by adjusting k_1 and k_2 to fit the conversion–time lines of Figures 3 and 4. The rate constants thus obtained at different temperatures are presented in Figure 5 and are further correlated by the Arrhenius law. The calculated equilibrium constants from k_1 and k_2, and those from the experimental measurement [cf. eq. (3)], are given in Figure 6 in the form of the van't Hoff law. The quantitative representation of the data by the two laws is internally con-
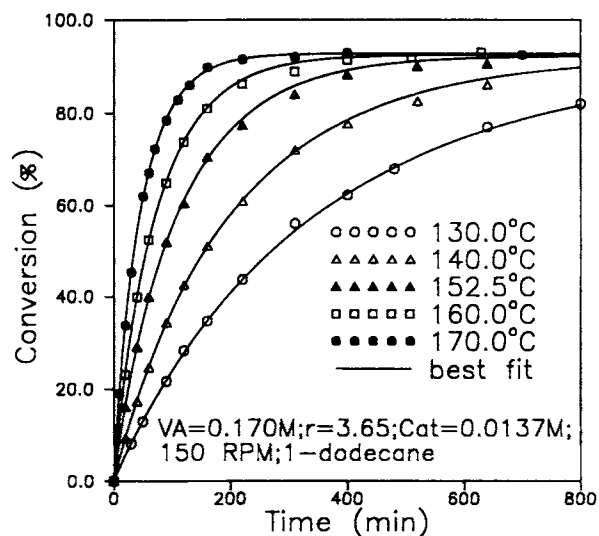

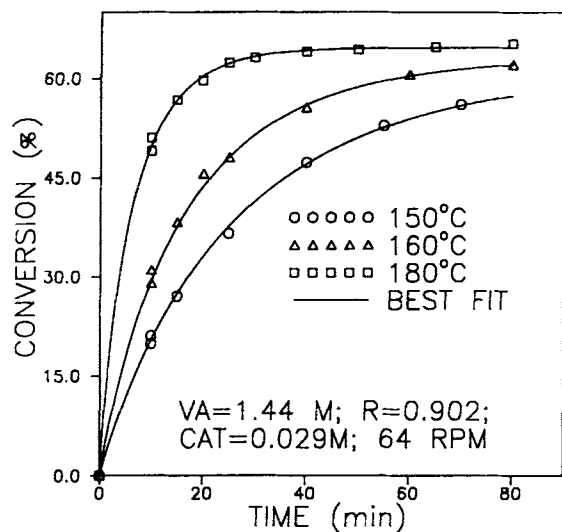**Figure 3**   Conversion as a function of time in solution.

Figure 4 Conversion as a function of time in the bulk.

Figure 6 Temperature dependence of K_e in solution and in the bulk.

sistent and appears to describe the reaction, in both solution and bulk, satisfactorily.

The data also show that the reaction in solution and in the bulk follows the same mechanism, both the overall forward and reverse reaction rates being linearly proportional to the concentrations of the ester group and the alcohol group (as they should).

The apparent rate constants are substantially higher in the bulk, due to the higher catalyst concentration, but the equilibrium constants are almost identical.
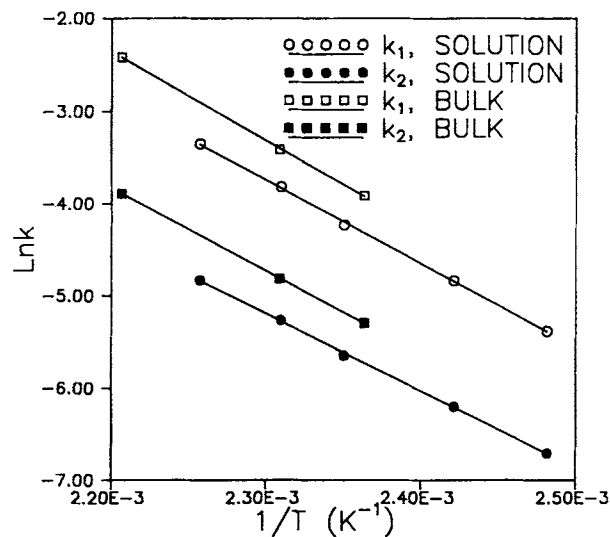

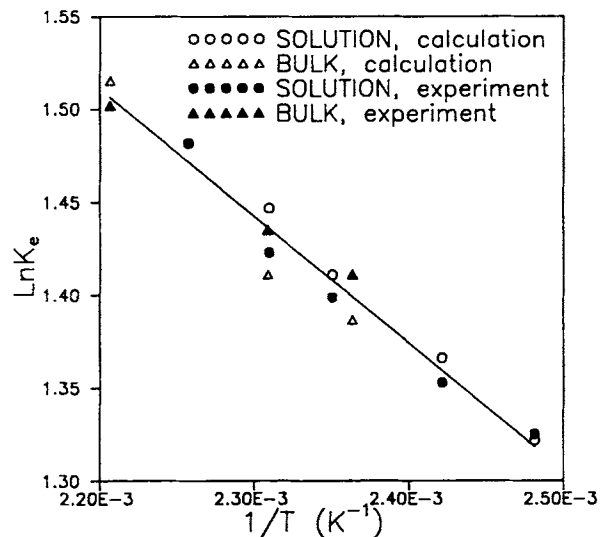**Figure 5** Temperature dependence of k_1 and k_2 in solution and in the bulk.

The dependencies of k_1 and k_2 on the catalyst concentration for both types of reaction media are described below.

Effect of the Catalyst Concentration on the Overall Reaction

Figure 7 shows the apparent rate constants k_1 and k_2 at various catalyst concentrations in solution and in the bulk. In both cases, the experimental results can be satisfactorily correlated by the following equations:

Solution (152.5°C): $k_1 = 0.117[\text{Cat}]^{0.485}$;

$$k_2 = 0.0309[\text{Cat}]^{0.499}$$

Melt (150°C): $k_1 = 0.112[\text{Cat}]^{0.489}$;

$$k_2 = 0.0285[\text{Cat}]^{0.491}$$

All rate constants have the dimension of [mol L/min].

It is important to note that in both cases, the rate constants k_1 and k_2 are roughly proportional to the square root of the catalyst concentration, indicating that the catalytic mechanism in solution and in the bulk is identical. The catalytic index is close to 0.5, which suggests that in all likelihood DBDTDL is converted into a dialkoxide in order effectively to catalyze the transesterification reaction, while both
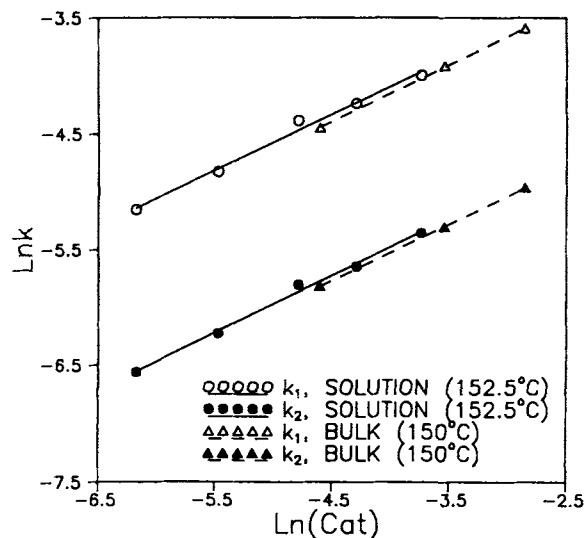
Figure 7 Catalyst concentration dependence of k_1 and k_2 in solution and in the bulk.
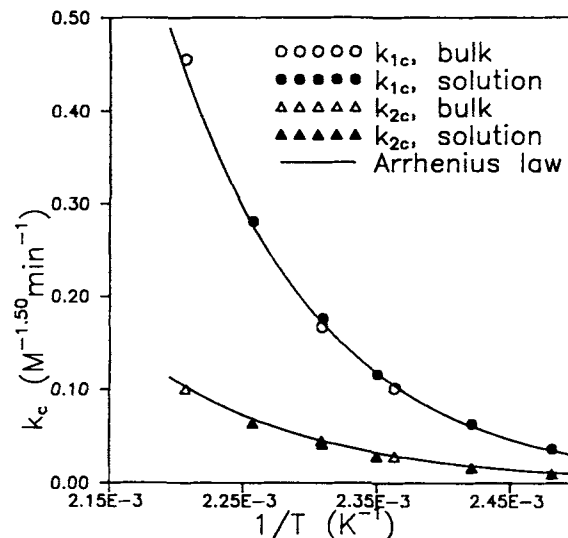

Figure 8 Temperature dependence of k_{1c} and k_{2c} in solution and in the bulk.

alkoxyl groups of the generated dialkoxide participate in the catalysis.

Direct Kinetic Comparison between Solution and the Melt

We have seen that the reaction carried out in solution and in the bulk follows the same mechanism: the overall forward and reverse reaction rates are linearly proportional to the concentrations of the ester group and the alcohol group, and to the square root of the catalyst concentration. The equilibrium constants match closely.

To make a direct comparison between the respective kinetic data sets obtained in solution and bulk, Figure 8 shows the intrinsic rate constants k_{1c} and k_{2c} (normalized k_1 and k_2 by the square root of the catalyst concentration). Table II lists the corresponding thermodynamic data of the reaction.

The "intrinsic" rate constants, k_{1c} and k_{2c}, of Figure 8, obtained from our measurements in the presence and absence of solvent, fall on the same re-

spective curves and further confirm the invariant nature of the overall apparent mechanism of the transesterification reaction with respect to the presence of inert solvents. The observable differences in the reaction time in bulk and in solution are due the differences in the molar concentration of the reactants.

Effect of Mechanical Mixing on the Overall Reaction

It may be somewhat surprising that the similarity between the kinetic results from the bulk and solution experiments is not masked, at least in part, by the five orders of magnitude difference in viscosity between the two systems. Evidently, neither the effect of viscosity on the diffusivity nor on the macroscopic mixing is significant within the time scale of the chemical reaction.

This finding can be made plausible by comparing the rate time scales of the chemical reaction and molecular diffusion, since in both systems the al-
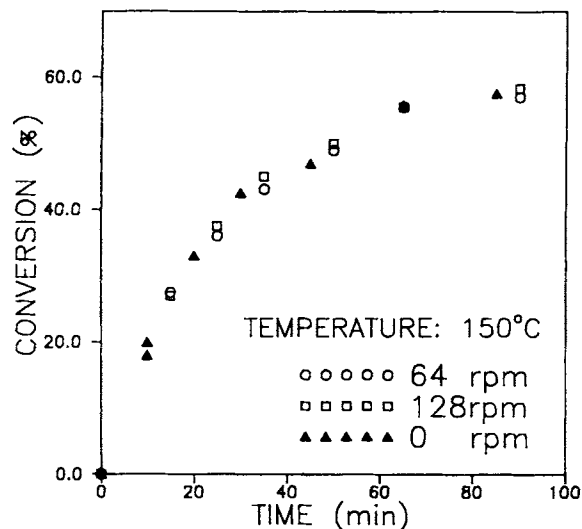
Table II Thermodynamic Data of the Reaction

	ΔE_1 [a]	ΔE_2 [a]	ΔH^0 [b]	ΔS^0 [c]	ΔH^0_{ave} [b]	ΔS^0_{ave} [c]
Solution	18.0	16.6	25.7	5.93	25.0	5.69
Melt	19.0	17.9	22.3	4.59		

[a] Kcal/mol.
[b] J/mol.
[c] KJ/mol*K°.
Subscript ave = average value derived from Figure 6.

Figure 9   Mixing effect on the overall reaction rate in the bulk.

cohol concentration was below the solubility limits. The characteristic reaction time, $t_R = 1/\{k_1a[3r + 1 - 2p_e(r + 1)]\}$, when compared to the characteristic diffusion time, $t_D = h^2/D$, appears to be large. Both the mixing length, h, and diffusivity, D, are functions of viscosity; even in the bulk (where a and h tend to be relatively large and D small) the ratio t_R/t_D is still much larger than unity during the transesterification reaction.*

CONCLUSIONS

In this article, we have presented the kinetics of the transesterification reaction of poly(ethylene-co-vi-

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* The lack of competition for the reactant molecules between the reaction and molecular diffusion is further brought out in Figure 9. During the bulk experiments, after the initial premixing at 64 rpm over three min, the reaction was allowed to proceed in three different modes: without additional mixing, at the same mixing speed, and at twice the rate of stirring. The initial premixing reduced the mixing length to be traversed by the reactants to a sufficiently small scale, so that no subsequent mixing was necessary.

nyl acetate) with alcohols in solution and in the bulk. It has been found that the chemical behavior (kinetics and equilibrium state) of 1-octanol, 2-ethyl 1-hexanol, and 3-phenyl 1-propanol towards the vinyl acetate groups is the same in bulk and in solution.

It has also been shown that, regardless of the reaction medium chosen, the reaction is reversible, and follows the same, second-order mechanism. The overall reaction rate for the forward or reverse reaction is linearly proportional to the respective concentrations of the ester and alcohol groups, and to the square root of the concentration of the catalyst (dibutyl tin dilaurate). While the reaction proceeds much faster in the bulk, a thorough comparison has revealed that the kinetics in solution and in the bulk are indistinguishable, despite the significant differences in viscosity and reactant concentrations.

The close agreement between the respective kinetic constants obtained in the presence and absence of a solvent has been attributed to the relatively low reaction rate, as compared with the rate of diffusion.

It has also been concluded that for this homogeneous reacting system, mechanical mixing is important only for the homogenization of the system at the initial stage of the reaction. Once this is achieved, no more mixing is necessary.

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