Catalysis and reactivity of the transesterification of ethylene and alkyl acrylate copolymers in solution and in the melt

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The transesterification of three ethylene and alkyl acrylate random copolymers (alkyl = methyl, ethyl and n-butyl) with 3-phenyl 1-propanol (PPOH) was studied in 1,2,4-trichlorobenzene solution and in the melt. Various catalysts were used, with dibutyltin dilaurate (DBTDL) and dibutyltin oxide (DBTO) showing the highest activities. The reaction between the poly(ethylene-*co*-methyl acrylate) and PPOH in solution in a closed reactor confirmed that this reaction is reversible. When operated in the melt in a semi-open batch mixer at temperatures between 170 and 190°C the equilibrium was totally shifted to the product side due to effective removal of the lighter alcohols generated from the reaction. The mechanism and rate constants of reaction are identical, regardless of the reaction medium chosen. The reactivity of an alkyl acrylate group towards PPOH depends, to a large extent, on the chemical structure of the alkyl group, and it follows the order: methyl > ethyl > n-butyl. This is primarily attributed to the fact that the longer the alkyl group, the lower the electrophilicity of the carbonyl carbon of the acrylate, and the higher the steric hindrance, both being detrimental to the reactivity. The steric hindrance argument is supported by the activation energies observed in the presence of DBTO as the catalyst: 69.0, 81.6 and 96.6 kJ mol^{-1} for the methyl, ethyl and n-butyl, respectively. Mechanical mixing favoured the reaction rate.

(Keywords: transesterification; copolymers; alcohols)

INTRODUCTION

Traditionally, it has been common practice to run chemical reactions involving polymers (polymerization or chemical modification) in the presence of a solvent. How to choose an adequate solvent for a given reaction has been one of the major research interests of chemists. Over the last three decades and because of the increasing demand for high-performance and cost-effective polymeric materials and the ever-growing concern about the environmental impact of excessive use of solvents, reactions have increasingly been run in solventless polymer melts using polymer processing machines, such as batch mixers and screw extruders, as reactors. The term 'reactive processing of polymers' that summarizes well this specialty has emerged in the polymer science and engineering community[1,2], and intense activity both in academia and in industry largely testifies to its ever-increasing importance[3–5]. Despite the fact that this new specialty has been practised to an appreciable degree in industry for the aforementioned reasons, the absence of solvent raises numerous fundamental problems that remain poorly understood. Just from the viewpoint of chemistry, the absence of solvent brings about complications caused by the high viscosity of polymer melts: heterogeneity of the reacting media, slow diffusion of reactants, etc., rendering difficult a proper control over the selectivity and the rate of reaction. As screw extruders have been the most frequently used continuous reactors where temperatures are high and reaction times are short (usually less than 10 minutes), effective catalysis is also very important for attaining high conversions.

In our continuing effort to understand the mechanism of chemical reactions in polymer melts and to search for new functional groups incorporated in commercial polymers with reactivities high enough for reactive extrusion, we reported the reactivity of methyl acrylate inserted randomly in a styrene or an ethylene copolymer towards small amines in solution and in the melt[6,7]. Overall, the reactivity of this type of reaction is low, even in the presence of 2-pyridone, a tautomeric compound that was the most effective catalyst of the many tested. This paper investigates the reactions of the same or other similar acrylates bound to a polyethylene backbone with small alcohols in solution and in the melt. The transesterification of an alkyl acrylate copolymer with an alcohol is expected to convert the alkyl acrylate into a new acrylate through the following mechanism:

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where R is an alkyl group; *a* and *b* denote the initial molar concentration of the alkyl acrylate and that of the reactant alcohol, respectively; *p* is the conversion with respect to the formation of the new alkyl acrylate.

A literature survey revealed little information on reactions between polymer-supported acrylic esters and alcohols, particularly in the molten state. Nevertheless, the reaction between an ester and an alcohol is largely known in organic and polymer chemistry. Additionally, our previous work[8–10] on the transesterification of ethylene and vinyl acetate copolymers with alcohols in solution and in the melt had provided a basis for this study.

EXPERIMENTAL

Materials

Three commercial grade (Elf Atochem, France) ethylene and alkyl acrylate random copolymers used in this study were: poly(ethylene-*co*-methyl acrylate) (EMA), poly(ethylene-*co*-ethyl acrylate) (EEA) and poly(ethylene-*co*-butyl acrylate) (EBA). They contained 33.8, 8.0 and 25.9% by weight of acrylate, respectively. Their number mass molecular weights measured by gel-permeation chromatography were about 25 000 g mol^{-1} with a polydispersity between 4 and 5. The model alcohol chosen was 3-phenyl 1-propanol (PPOH), as it has a relatively high boiling point (235°C at 760 mmHg) and a benzene ring. The latter allows easy follow-up of the reactions by i.r. and u.v. spectroscopy. Various catalysts were used. Selected properties of the small species are shown in *Table 1*. All reactants were used as received.

Reaction procedures

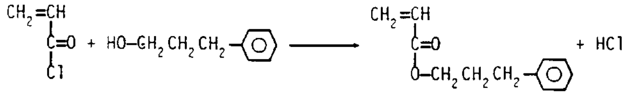
Reactions in 1,2,4-trichlorobenzene were performed in a closed stainless steel reactor, and those in the melt in a batch mixer (Haake Rheocord). In the first case, about 10 wt% copolymer was charged, and in the second case 40 g of a copolymer and given amounts of the alcohol (8–12 g) and a catalyst (0.2–1.5 g) were introduced into the mixing chamber (50 cm^3) which was preheated to a desired temperature (between 170 and 190°C). The mixing speed of the two rotors was fixed at 64 rev min^{-1}, unless indicated otherwise. Samples were collected from the mixer at chosen time intervals (between 15 and 90 min) and quenched in liquid nitrogen in order to stop the reaction.

Purification of the products

Samples collected from the stainless steel reactor at chosen time intervals (between 1 and 25 h) were precipitated in acetone, dissolved in chloroform, reprecipitated in acetone, filtered and then dried in a vacuum oven. Those from the mixer were dissolved in chloroform, precipitated in acetone, redissolved in chloroform, reprecipitated in acetone, filtered and then vacuum-dried.

Synthesis of 3-phenyl 1-propyl acrylate monomer and its homopolymer

In order to characterize the reaction products, poly(3-phenyl 1-propyl acrylate) (PPPA) was synthesized from its monomer (PPAM). As the latter was not available commercially either, it was obtained by esterifying acryloyl chloride with PPOH in a stirred three-necked flask. The reaction scheme can be described as:



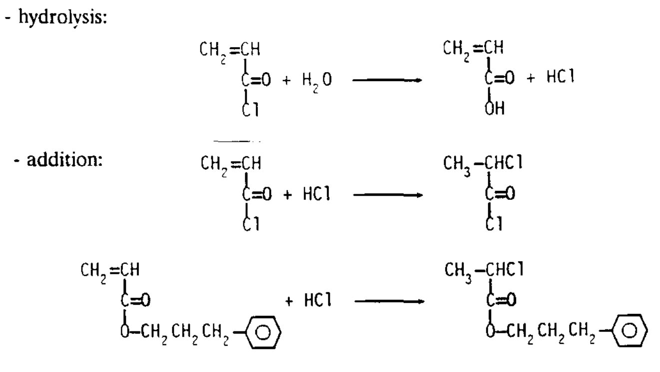
Besides the desired esterification, hydrolysis and addition

Table 1 Selected properties of the chemicals used in this study

Chemicals	Molecular weight (g mol^{-1})	Melting pt (°C)	Boiling pt (°C)	Purity (%)
$C_6H_5(CH_2)_3OH$	136.19	32–34	202	97
$H_2C{=}CHCOCl$	90.51	Liquid	72–76	98
$Bu_2SN(OOCC_{11}H_{23})_2$	631.56	Liquid	–	98
Bu_2SnO_2	248.92	300	–	98
Me_2SnO_2[a]	166.77	Solid	–	–
Ph_2SnO_2[a]	288.90	Solid	–	–
$Ti[O(CH_2)_3CH_3]_4$	340.36	Liquid	–	99
$(C_4H_9O)_2Ti(CH_3COCHCOCH_3)_2$	378.24	Liquid	–	–
$(CH_3CO_2)_2Zn.2H_2O$	219.5	Solid	–	>98
$(CH_3CO_2)_2Co.4H_2O$	249.08	Solid	–	–
Sb_2O_3	291.50	665	–	>99
$NaOCH_3$	54.02	300	–	95
NaOH	40.00	Solid	–	>97
$p\text{-}CH_3C_5H_4SO_3.H_2O$	190.22	103–106	–	99
2-Pyridone	95.10	105–107	280–281	97
1,2,4-Trichlorobenzene	181.45	16	214	>99[b]
Chloroform	119.38	−63	61	99.8[c]
$CH_3(CH)_{14}CH_3$	226.45	Liquid	–	>99[b]

[a] All reactants were purchased from Aldrich except Me_2SnO_2 and Ph_2SnO_2 (purchased from Stream)
[b] Anhydrous
[c] A.C.S. reagent for purification and A.C.S. spectrophotometric grade for u.v. analysis

reactions could occur:



In order to minimize the side reactions, precautions were taken: the temperature was kept below 5°C; PPOH was gradually added into the flask in order to avoid violent heat generation; the reaction system was purged with nitrogen gas to prevent moisture and to help the removal of the generated HCl. On the other hand, PPOH was in excess in order to deplete completely the acryloyl chloride. After reaction for 5 h, the mixture became two separate liquid phases, the lower one being the PPAM. After an intensive washing with a dilute aqueous sodium hydroxide solution, the PPAM was collected and then polymerized at 70°C using 1% AIBN as the initiator. The corresponding homopolymer obtained after 10 h was purified and vacuum dried.

Analysis

The PPPA was characterized by elemental analysis, gel-permeation chromatography (g.p.c.), differential scanning calorimetry (d.s.c.), Fourier transform infra-red spectroscopy (*FT*i.r.) and ultra-violet spectrophotometry (u.v.). The modified alkyl acrylate copolymers were analysed by u.v. and *FT*i.r.

RESULTS AND DISCUSSION

Characterization of the PPPA

As the PPPA is a novel polymer, it was characterized using various techniques. The compositions of the elements in the PPPA measured by elemental analysis were in good agreement with the theoretical ones (*Table 2*). The average number and weight mass molecular weights of the PPPA measured by g.p.c. are 21 000 g mol^{-1} and 40 000 g mol^{-1}. The glass transition temperature (T_g) measured using d.s.c. (Perkin–Elmer 4) with a scanning rate of 10°C min^{-1} between -80 and 100°C was -17.0°C. The u.v. spectrum in chloroform at room temperature revealed four major peaks between 240 and 290 nm: 253, 259, 261 and 268 nm, with the strongest one at 259 nm. This u.v. spectrum is virtually identical to that of polystyrene, as expected. A plot of the absorbance of the maximum peak, A, *versus* the molar concentration, c, of the 3-phenyl 1-propyl acrylate moiety (PPAG) in the PPPA showed that the experimental points could be well correlated with a straight line, being in accordance with the Lambert–Beer law. The slope of the straight line gave an extinction coefficient of 224.0 M^{-1} cm^{-1}, which again is very close to that of polystyrene (222.5 M^{-1} cm^{-1}) in the same solvent.

The i.r. spectrum of the PPPA was collected by casting a solution on a NaCl disc between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1}. *Figure 1* focuses this spectrum on zone 2110–600 cm^{-1}. The ν(C–H) peaks of the benzene ring appear at 3106, 3085, 3062, 3026 and

Table 2 Calculated and measured compositions of the PPPA

	Composition (%)		
	C	H	O
Calculated	75.8	7.4	16.8
Measured	75.5	7.4	17.1

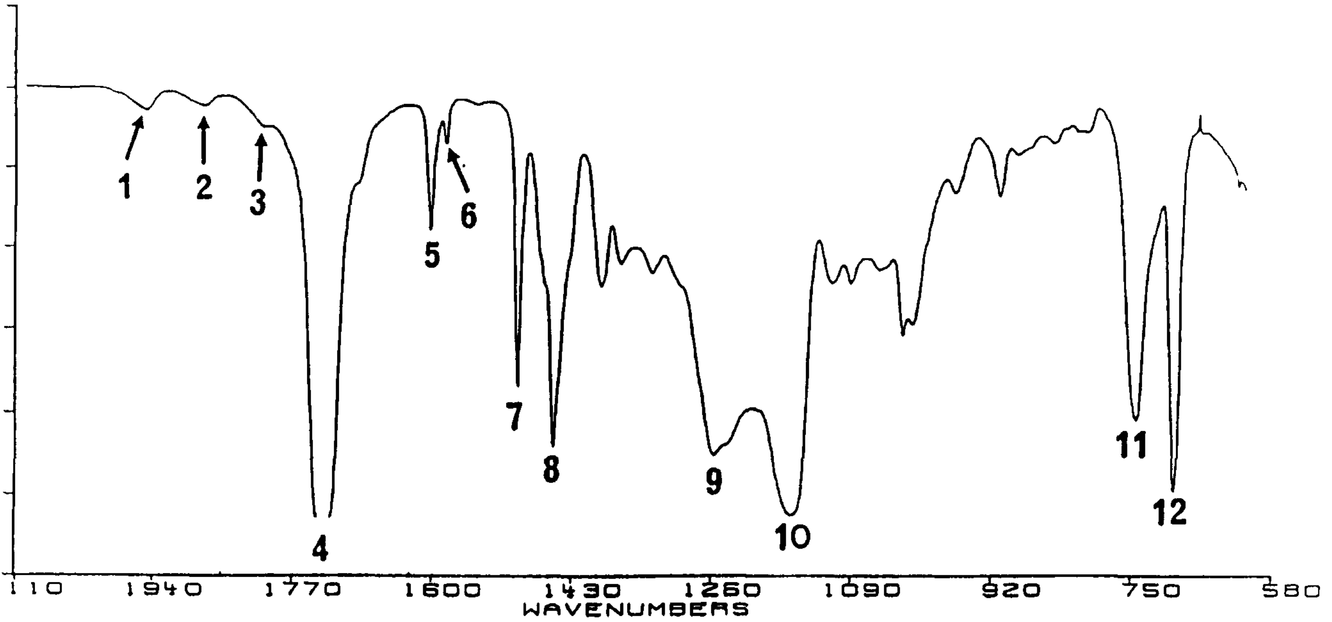


Figure 1 I.r. spectrum of PPPA between 2110 and 600 cm^{-1}, recorded with a NaCl disc

3002 cm^{-1}, and those of the aliphatic bonds between 2980 and 2820 cm^{-1}. For the sake of simplicity, the characteristic peaks of the benzene ring and the acrylate between 2110 and 600 cm^{-1} are gathered in *Table 3*. Overall, the spectrum of this polymer is an overlap of the spectrum of polystyrene and that of poly(n-propyl acrylate). In fact, the i.r. spectrum of this novel polymer was put in Hummel's i.r. data base.

In sum, the various characterization techniques confirm the anticipated chemical structure of the PPPA.

Characterization of the modified alkyl acrylate copolymers

An i.r. spectrum of the EMA copolymer modified in solution was made by casting its solution on a NaCl disc. In comparison with the original EMA copolymer (*Figure 2*), the modified one yields at least three additional peaks located at 5, 7 and 12, characteristic of the benzene ring (see *Table 3*). The i.r. spectrum of the EMA copolymer modified in the melt was identical to that in solution, implying that the formulated transesterification proceeds in the same manner, regardless of the reaction medium chosen. Also worthy of mention is that the i.r. spectra of the EEA and the EBA copolymers before and after reaction were very similar, respectively, to those of the EMA copolymer before and after modification, and that the u.v. spectra of the modified EMA, EEA and EBA copolymers were identical to that of the PPPA.

Table 3 Characteristic peaks of the PPPA. Catalytic concentration: 0.0244 M; 180°C for 50 min

Peak (cm^{-1})	Mark	Wavenumber (cm^{-1})	Assignment
1960–1920	1	1949	Overtones + combinations for Ph–R
1920–1855	2	1878	
1855–1750	3	1802	
1750–1725	4	1735	ν(CO)
1625–1590	5	1604	ν(C=C)
1590–1575	6	1584	
1510–1475	7	1497	
1475–1440	8	1454	δ(CH)
1275–1185	9	1258	ν(CO), $\mathrm{C\underline{OO}C}$
1210–1050	10	1164	ν(CO), $\mathrm{CO\underline{OC}}$
770–730	11	747	ν(CH) for Ph–R
710–690	12	700	

To sum up, the information provided by the i.r. and u.v. spectroscopy confirms the formulated chemistry of the transesterification, and no side reactions were observed.

Determination of the reaction conversion

The u.v. was used to measure the conversion of the transesterification, as the molar extinction coefficient of the PPAG in the PPPA was measured, and it was believed to be the same in all three modified copolymers. However, a technical problem was encountered for the EEA copolymer, as it was soluble in chloroform only at a temperature close to the boiling point because of a much lower acrylate content. Thus hot hexadecane (above 100°C) was used to dissolve it, requiring additional precautions to be taken: insulation of the u.v. sample cell and correction for the thermal expansion effect on concentration. I.r. spectroscopy is more convenient in this regard as it works well with thin films, and its sensitivity also seems to be higher, but a quantitative characterization using i.r. needed modified copolymer samples of known contents in PPAG, which in our case were made possible using the u.v. results. For the i.r. analysis, the peak at 1604 cm^{-1} was chosen as the target and the shoulder peak at 2680 cm^{-1} as the internal reference. If R denotes the ratio of A_{1604} to A_{2680} (A_{1604} and A_{2680} are the absorbances of the peaks at 1604 and 2680 cm^{-1}), then it should be proportional to the ratio of the number of the PPAG over that of the ethylene unit according to the Lambert–Beer Law:

$$R=\frac{A_{1604}}{A_{2680}}=k'\frac{wp/M_{\mathrm{A}}}{1-w/M_{\mathrm{E}}}=k'\left(\frac{M_{\mathrm{E}}}{M_{\mathrm{A}}}\right)\left(\frac{wp}{1-w}\right) \qquad (1)$$

where M_{A} and M_{B} denote the molecular weight of the original alkyl acrylate and that of the ethylene moiety,

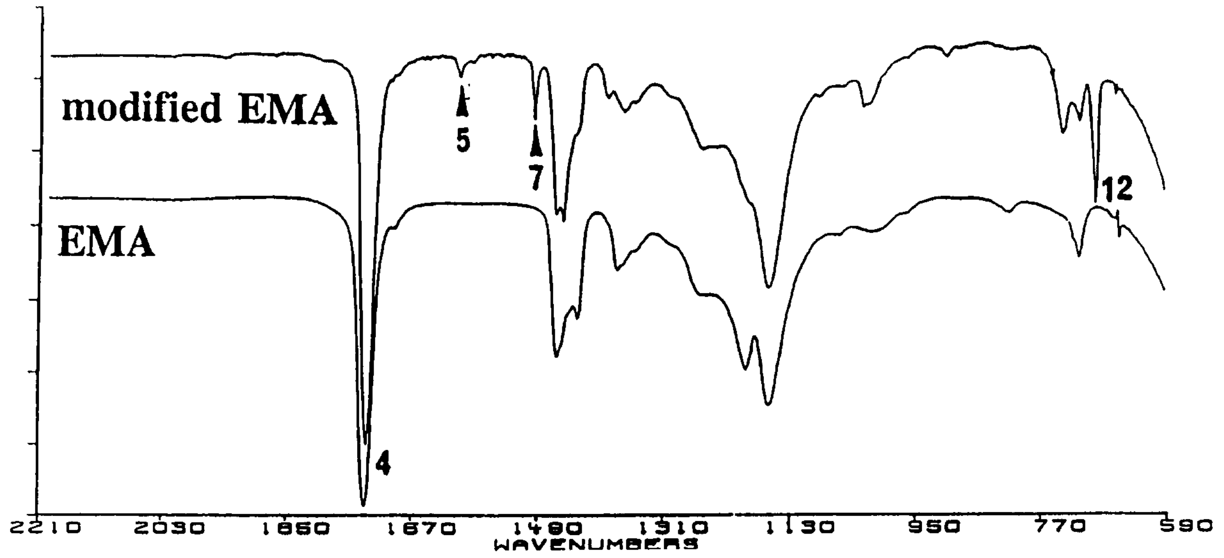


Figure 2 I.r. spectra of the EMA copolymer before and after reaction with PPOH (recorded with a NaCl disc)

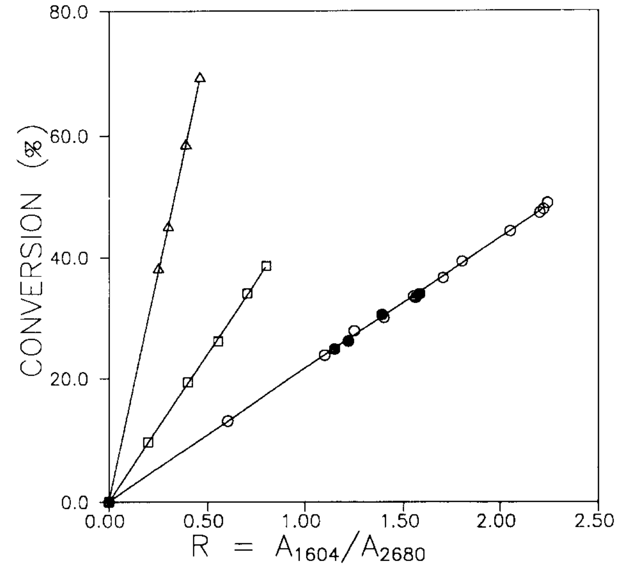


Figure 3 Conversion determined by u.v. *versus* $R(A_{1604/2680})$ for the modified EMA, EEA and EBA copolymers with PPOH. ○, EMA (solution); ●, EMA (bulk); △, EEA (bulk); □, EBA (bulk)

Table 4 Characteristic data of the modified copolymers

Copolymer	Wt%	M_A(g mol^{-1})	k	k'
EMA	33.8	86.1	21.64	0.276
EEA	8.0	100.1	150.1	0.274
EBA	25.9	128.2	48.23	0.272

respectively; w is the initial weight percentage of the original alkyl acrylate in an ethylene and alkyl acrylate copolymer, and k' is a constant.

Rearrangement of equation (1) gives

$$p=\left(\frac{M_A}{k'M_E}\right)\left(\frac{1-w}{w}\right)R=kR \qquad (2)$$

This equation implies that for all three ethylene and alkyl acrylate copolymers, the conversion is a linear function of R, characterized by a constant k. The constant k depends only on the nature of the acrylate, namely, w and M_A, whereas k' should be a universal constant for all three copolymers.

Figure 3 plots the conversion (p), measured by u.v., *versus* R for all three modified copolymers. For each of them, p is indeed a linear function of R. Particularly noteworthy is that the results obtained from the samples of the modified EMA in the melt match well those from the solution, confirming again that the reaction products are identical, regardless of the reaction medium chosen. *Table 4* shows the coefficients k and k' for all three copolymers, showing that while the k values are different for these copolymers, the k' values are the same within experimental scatters. The latter finding is very useful, as it implies that in practice, one calibration curve by the u.v. technique using any one of the copolymers is enough.

Catalytic activity of various compounds

This was examined in the melt by measuring the conversions of the methyl acrylate of the EMA copolymer into PPAG at given reaction conditions, *Table 5*. It is seen that:

1. Virtually no anticipated reaction takes place without any catalyst.
2. $NaOCH_3$, which is a strong base and a very powerful catalyst for the conversion of the vinyl acetate of a poly(ethylene-*co*-vinyl acetate) (EVA) into the vinyl alcohol through transesterification with a paraffinic alcohol[8], does not show its activity in this reacting system. Also observed is the weak activity of NaOH, which is frequently used as a basic catalyst for the transesterification of small molecules.
3. *p*-Toluenesulfonic acid, used frequently as an acidic catalyst for the transesterification of small molecules, shows an interesting activity.
4. The activity of 2-pyridone is very weak, despite the fact that it is a very good catalyst for the aminolysis of the EMA copolymer with an amine[6,7], a reaction apparently similar to the present one.
5. The catalytic activities of zinc acetate, cobalt acetate and antimony(III) oxide are undetectable. This is rather surprising, as they are high for the synthesis of polyesters (e.g. PET and PBT) by transesterification. The explanation would be that these catalysts hardly react with the reactant alcohol to form the corresponding dialkoxides, which were confirmed to be the real catalysts[9]. While $Ti(OBu)_4$ quickly leads to crosslinking, similar to that observed in the transesterification of EVA[9], titanium(IV) di-n-butoxide-*bis*(acetyl-acetonate) does show an appreciable activity.
6. Among the four organo-tin compounds tested, DBTDL and DBTO show the highest activities. This was also found in the transesterification of the EVA system[9].

A more detailed comparison of the activity of the tin derivatives was made by following up the conversion as a function of reaction time under the same reaction conditions in the mixer, *Figure 4*. Over the full time-scale, the activity follows the order: DBTO > DBTDL > DMTO ≫ DPTO, indicating that the activity of an organometallic compound depends not only on the nature of the metallic atom, but also on the organic substituent. The latter is better illustrated when comparing DBTO, DMTO and DPTO, the chemical structures of which differ only in the organic part. The activity difference

Table 5 Activity comparison of the EMA/PPOH system between DBTDL and DBTO. Catalytic concentration: 0.0244 M; 180°C for 50 min

Catalyst	p(%)
None	≅0
NaOH	<1
$NaOCH_3$	<1
2-Pyridone	<1
p-$CH_3PhSO_3.H_2O$	15.9
Sb_2O_3	<1
$(CH_3CO_2)_2Zn.2H_2O$	<1
$(CH_3CO_2)_2Co.4H_2O$	<1
$Ti[O(CH_2)_3CH_3]_4$	Crosslinking
$(C_4H_9O)_2Ti(CH_3COCHCOCH_3)_2$	32.5
DBTDL	31.0
DBTO	37.8
DMTO	26.4
DPTO	6.2

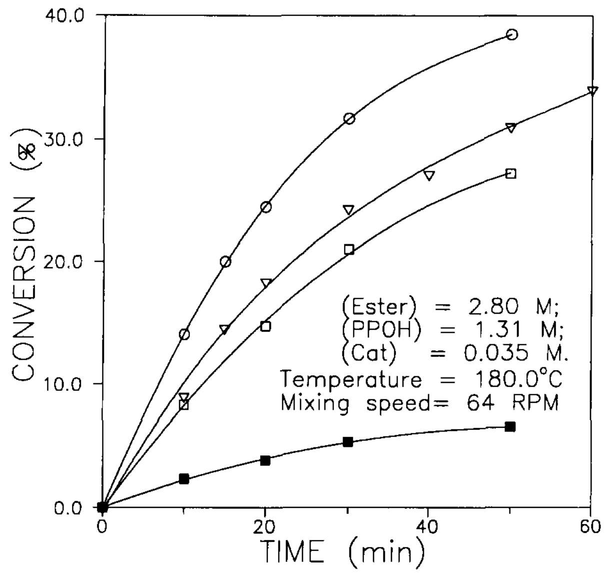


Figure 4 Conversion *versus* time in the presence of various tin catalysts at 180°C. ○, DBTO; ▽, DBTL; □, DMTO; ■, DPTO

among these compounds is thought to be related to the difference in the electron-donating capacity of the substituent: n-butyl > methyl ≫ phenyl. Several methods were proposed in the literature to relate the activity to the nature of the catalyst, as summarized in a previous work[9]. One of the empirical methods, based on the results of the synthesis of polyesters by transesterification, is to relate the catalytic activity of an organometallic compound to the electronegativity of the metallic compound[11,12]. According to this relationship, tin derivatives are less effective than titanium or zinc derivatives. Moreover, as the electronegativity of a metallic atom is supposed to be the same in its derivatives independent of the nature of the organic substituent[13], the tin derivatives used in this study should have the same activity. Our results do not show this relationship. Another method is to relate the activity to the complexation capacity of the organometallic compounds[14,15]. While this method appears to be more convincing, it gives results similar to the previous one. Being consistent with the arguments in ref. 9, our results can only be reasonably well explained by the catalytic mechanism proposed therein for this type of catalyst, that an intermediate product (a dialkoxide) generated from a reaction between the alcohol and a tin compound be the real catalyst. Thus, the higher is the electron-donating capacity of the organic substituent, the higher the nucleophilicity of the alkoxy group of the real catalyst, and the higher the catalytic efficiency.

Kinetic comparison of the EMA/PPOH system in solution and in the melt

It was proposed and confirmed previously[9,10] that the mechanism of the transesterification of an EVA copolymer with alcohols in solution and in the melt is the same, and the overall reaction rate, V, is expressed by

$$\begin{aligned} V &= \mathrm{d}[\text{vinyl alcohol}]/\mathrm{d}t \\ &= k_{1\mathrm{c}}[\text{Cat}]^{0.5}[\text{vinyl acetate}][\text{alcohol}] \\ &\quad - k_{2\mathrm{c}}[\text{Cat}]^{0.5}[\text{vinyl alcohol}][\text{new acetate}] \\ &= k_{1\mathrm{c}}[\text{Cat}]^{0.5}(a-ap)(b-ap) - k_{2\mathrm{c}}[\text{Cat}]^{0.5}(ap)(ap) \end{aligned} \tag{3}$$

where k_{1c} and k_{2c} denote the intrinsic forward and reverse reaction constants, respectively, and Cat is either DBTDL or DBTO. Defining a functional ratio $r = b/a$, equation (3) reduces to

$$\mathrm{d}p/\mathrm{d}t = k_1 a(1-p)(r-p) - k_2 a p^2 \tag{4}$$

with $k_1 = k_{1c}[\text{Cat}]^{0.5}$ and $k_2 = k_{2c}[\text{Cat}]^{0.5}$.

The equilibrium constant K_e can be calculated by equation (5) once the conversion at equilibrium is known, or by equation (6) from the apparent forward and reverse reaction constants, k_1 and k_2.

$$K_e = \frac{p_e^2}{(1-p_e)(r-p_e)} \tag{5}$$

$$K_e = k_1/k_2 \tag{6}$$

Integration of equation (4) yields

$$\frac{1}{a\Delta}\ln\left[\frac{2(1-1/K_e)p-(1+r)+\Delta}{2(1-1/K_e)p-(1+r)-\Delta} \times \frac{\Delta-(1+r)}{\Delta+(1+r)}\right] = k_1 t \tag{7}$$

where $\Delta = \sqrt{(1+r)^2 - 4(1-1/K_e)^2}$; $r \neq 1$.

In the subsequent sections, this reaction mechanism and the corresponding rate equations will be used to explain the results generated in this study. In contrast to the transesterification of an EVA copolymer with an alcohol where the small molecule reaction product is an ester having a higher boiling point than the reactant alcohol, the reaction between any one of the acrylate copolymers used in this study with PPOH generates a lighter alcohol (methanol, ethanol or n-butanol) as the small molecule product. If the product alcohol can be effectively removed from the reacting system so that the reverse reaction is negligible, equation (7) reduces to

$$\frac{1}{a-b}\ln\frac{1-p}{1-p/r} = k_1 t \quad (r \neq 1) \tag{8}$$

The conversions obtained from the 1,2,4-trichlorobenzene solution and the melt are shown in *Figure 5*. A comparison between the two cases shows that the reaction proceeds much faster in the melt, despite a much

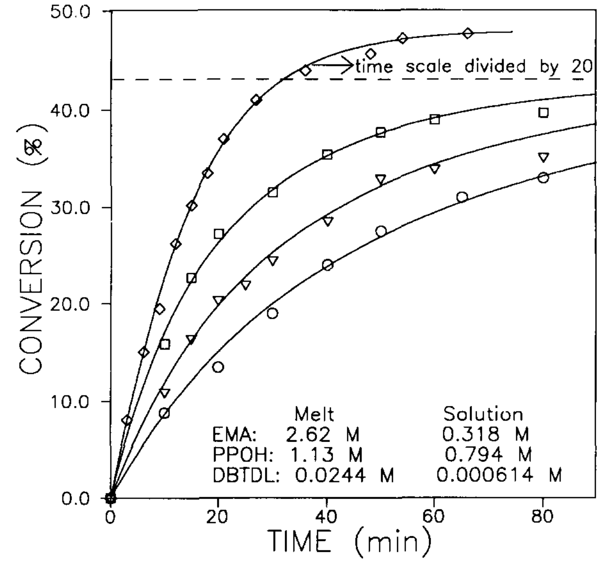


Figure 5 Conversion *versus* time for the EMA/PPOH/DBTDL system in 1,2,4-trichlorobenzene at 180°C and in the melt. The time-scale for the solution is divided by 20. (– – –) Maximum conversion possible (43%) imposed by [–OH]/[–COO] = 0.43. ○, 170°C, melt; ▽, 180°C, melt; □, 190°C, melt; ◇, 180°C, solution. (——), Best fit

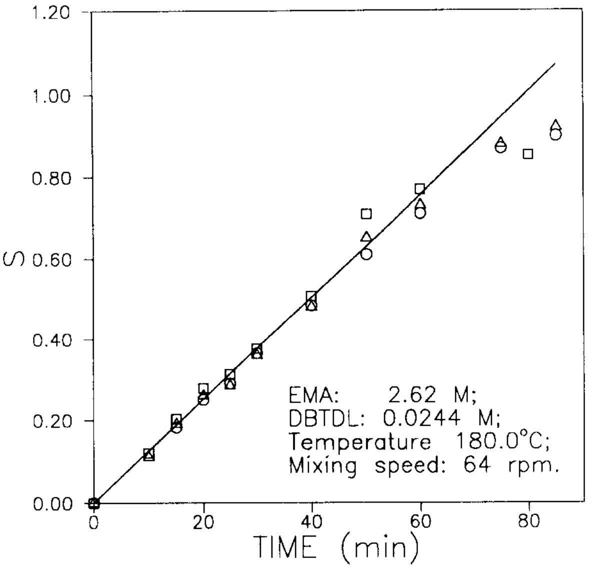


Figure 6 Plot of the left side of equation (8) *versus* time of the EMA/PPOH/DBTDL system in the melt for three different concentrations of PPOH at 180°C. ○, $r=0.332$; □, $r=0.430$; △, $r=0.527$. Average $k_1=0.0126$

lower functional ratio, 0.43 against 2.5 in solution. For example, after 60 min of reaction at 180°C, 33.5% conversion is obtained from the melt and only a few per cent from the solution. It should also be noted that while the conversion reaches an equilibrium value in solution (47.7% after 40 h), the reaction in the melt seems to be complete. The latter is not surprising as the methanol, once generated from the reaction at high temperatures (between 170 and 190°C), forms bubble nuclei instantaneously, and then gets out of the molten reacting system rapidly so that the equilibrium is shifted to the product side. While the reversibility of this reaction was confirmed in solution by the observation that a plot of the left side of equation (7) *versus* time yielded a straight line for the conversions, the pseudo-irreversibility of this reaction in the melt was demonstrated by the fact that a plot of the left side of equation (8) *versus* time using the conversions in the melt gave straight lines. The full lines in *Figure 5* show the quality of fit of the back-calculated conversion curves using the k_1 and k_2 values in solution, and the k_1 values in the melt, respectively. A visible deviation is noted between the calculated conversion curves and the experimental data at long reaction times and/or high temperatures in the melt, due probably to some loss of the PPOH. In the order to validate equation (8) further, the reaction in the melt was run at two other different initial concentrations of PPOH at 180°C. The kinetic data obtained were compared on the basis of equation (8) (*Figure 6*). The fact that all the experimental points fall on a single line, except at longer reaction times, implies that the overall reaction indeed behaves as an irreversible reaction, of which the overall rate is proportional to the alcohol concentration.

It would be interesting to compare the rate constants in solution and in the melt, as the overall reaction rate in the melt is much faster. As will be shown later, the apparent reaction constant of the reaction is proportional to the square root of catalyst concentration, thus the k_{1c} and k_{2c} values can be calculated (180°C): in solution, $k_{1c}=0.0730\,M^{-1.5}\,min^{-1}$; $k_{2c}=0.332\,M^{-1.5}\,min^{-1}$; in the melt, $k_{1c}=0.0807\,M^{-1.5}\,min^{-1}$. The k_{1c} values obtained from both media are viewed as the same within experimental error, confirming that the kinetic behaviour of this reaction is the same in both reacting media, and that a much faster reaction rate in the melt is simply due to much higher reactant concentrations. It follows that one of the advantages of the chemical reaction carried out in the melt is its high reaction rate due to much higher reactant concentrations. None the less, it is somewhat surprising that the similarity between the kinetic results from the solution and the melt is not masked, at least in part, by the large difference in viscosity (five orders of magnitude) between the two reacting media. Evidently, neither the time-scale of the diffusion nor that of the macro/micromixing in the melt is significant compared with the time-scale of the reaction. This argument can be made plausible. In the melt, where macro/micromixing and diffusion tend to play a more important role, the alcohol concentration was purposely chosen to be below its solubility limits where the macro/micromixing process appears to be very fast. On the other hand, the characteristic time of reaction, $t_R=1/k_1a$, when compared with that of diffusion, $t_D=h^2/D$, is very large, as the diffusion length, h, is small ($<10^{-7}$ m) and the diffusivity, D, is relatively high ($>10^{-8}\,m^2\,s^{-1}$).

Activity comparison between DBTO and DBTDL

The reactivity of the EMA/PPOH system in the melt was also studied using DBTO as the catalyst. Again, a good agreement was noted between the experimental data and equation (8). A plot of the apparent rate constant k_1 *versus* temperature on the basis of the Arrhenius law allowed the determination of the activation energies for DBTO and DBTDL. The activation energy is 69.0 kJ mol^{-1} for DBTO and 69.4 kJ mol^{-1} for DBTDL. The surprisingly close activation energies strongly confirm that DBTO and DBTDL catalyse the reaction in the same manner. A plot displaying the catalyst concentration dependence of k_1 at 180°C showed that over the entire concentration range, DBTO always displays a higher activity, in agreement with a previous work[9] concerning the transesterification of an EVA copolymer with an alcohol. This can be explained as follows: as the real catalyst is not DBTO or DBTDL, but an intermediate product (dialkoxide) generated from the reaction between the tin compounds and the reactant alcohol[9], when the same weight quantity of catalyst is used, the molar concentration of the real catalyst formed from DBTO is higher due to a lower mass molecular weight. Moreover, the reaction between the alcohol and DBTO releases water which can be effectively removed from the

Table 6 Catalytic activity comparison between DBTDL and DBTO

		Temperature (°C)		
	Catalyst	170	180	190
$k_1 \times 10^2$ ($l\,mol^{-1}\,min^{-1}$)	DBTDL	0.90	1.26	2.05
	DBTO	1.20	1.85	2.70
Catalyst concentration-dependence of k_1 (180°C)	DBTDL	$k_1=0.0848\,[DBTDL]^{0.523}$		
	DBTO	$k_1=0.0910\,[DBTO]^{0.492}$		
Activation energy	DBTDL	69.4 ± 6.1 kJ mol^{-1}		
	DBTO	69.0 ± 4.2 kJ mol^{-1}		

reacting medium, shifting the equilibrium to the dialkoxide side, whereas a heavy acid is formed from DBTDL, which cannot be removed. The dependence of k_1 on both tin compounds is found to be satisfactorily described by:

$$\text{DBTO:}\quad k_1 = 0.0910[\text{DBTO}]^{0.492}(\text{M}^{-1}\,\text{min}^{-1})$$

$$\text{DBTDL:}\quad k_1 = 0.0848[\text{DBTDL}]^{0.523}(\text{M}^{-1}\,\text{min}^{-1})$$

Note that the two exponents are very close to 0.5, the value suggested by the reaction mechanism[9].

Reactivity comparison between EMA, EEA and EBA

In addition to the EMA copolymer, the reactivity of the EEA and that of the EBA in the melt was examined using DBTO as the catalyst. Note first that the difference among these three copolymers in terms of the alcohol products lies in the fact that the EMA generates methanol, the EEA and the EBA yield ethanol and 1-butanol, respectively. Similar to the EMA/PPOH system, a good agreement was found between the experimental data and the best-fit curves of equation (8), indicating that the reactions of these two copolymers are also quasi-irreversible. The latter can only be explained by arguing that ethanol (b.p.: 78°C at 760 mmHg) and 1-butanol (b.p.: 118°C at 760 mmHg), like methanol in the case of the EMA copolymer, are also able to evaporate quickly from the molten reacting systems. *Figure 7* compares the reactivities of the EMA, EEA and EBA copolymers in terms of k_1 as a function of temperature ($1/T$). This can be expressed, respectively, by

$$\text{EMA:}\quad k_1 = 1.38 \times 10^5\,\text{e}^{-8325/T}$$

$$\text{EEA:}\quad k_1 = 3.83 \times 10^7\,\text{e}^{-9819/T}$$

$$\text{EBA:}\quad k_1 = 1.33 \times 10^9\,\text{e}^{-11626/T}$$

The reactivity follows: EMA > EEA > EBA, indicating that the longer the alkyl chain of alkyl acrylate, the weaker the reactivity. This can be explained by the fact that the longer the alkyl group, the lower the electrophilicity of the carbonyl carbon of the alkyl acrylate, and the higher the steric hindrance. The steric hindrance argument is supported by the activation energies observed: 69.0, 81.6 and 96.6 kJ mol^{-1} for the EMA, EEA and EBA, respectively.

The reactivities of the three acrylate copolymers towards alcohols in terms of conversion in the melt are very close to that of an EVA copolymer, despite much lower reaction constants[9,10]. This is because the equilibrium of the transesterification of an EVA copolymer can hardly be shifted by devolatilizing the generated ester, as it is always heavier than the reactant alcohol, whereas in the case of the acrylate copolymers, the product alcohols can be largely or totally removed, shifting the equilibrium to the product side. It is believed that the reactivities of these ethylene and alkyl acrylate copolymers are high enough for reactive extrusion processes.

Effect of mechanical mixing

Mechanical mixing in the batch mixer is believed to play, a priori, at least two important roles: homogenization of reacting mixtures through macro/micromixing, and renewal of interfaces when the components of the mixture are immiscible. For our particular reacting systems, mechanical mixing also accelerates the removal of the product alcohols, favouring the overall reactions. The results obtained from the melt so far were obtained at a mixing speed of 64 rev min^{-1}. In order to rationalize the mixing effect, the reaction between PPOH and the EMA, EEA or EBA copolymer was run under various mixing histories: after 5 min mixing at 64 rev min^{-1}, (1) the rotational speed of the rotors was either kept unchanged; or (2) increased to 90.5 rev min^{-1}; or (3) decreased to 0 rev min^{-1} for the rest of the reaction time. It was found that for all three reacting systems, a certain mixing speed is necessary in order to remove the product alcohols effectively. This is better illustrated by *Figure 8* where is shown the conversion as a function of time for the EBA system under the three mixing histories mentioned above. Clearly the reaction proceeds much more slowly without mixing, due to a much slower devolatilization rate of the 1-butanol. On the other hand, no appreciable difference is observed between mixing at

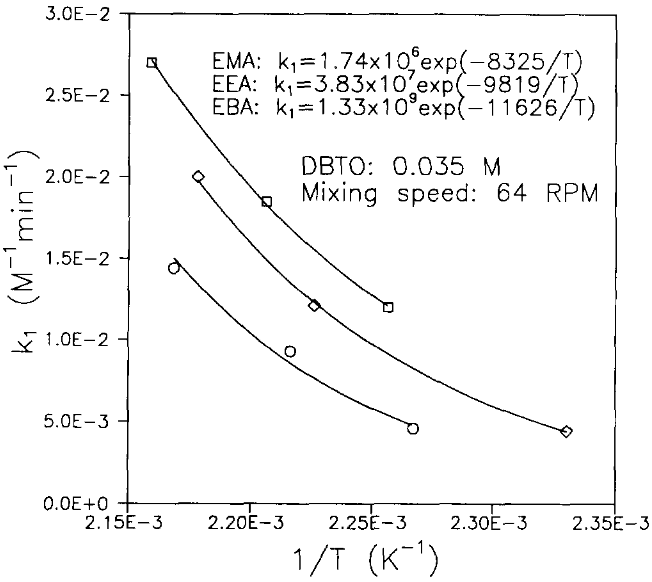


Figure 7 Reactivity comparison (k_1) of (□) EMA, (◇) EEA and (○) EBA towards PPOH in the melt in the presence of DBTO as the catalyst. (——), Arrhenius equation

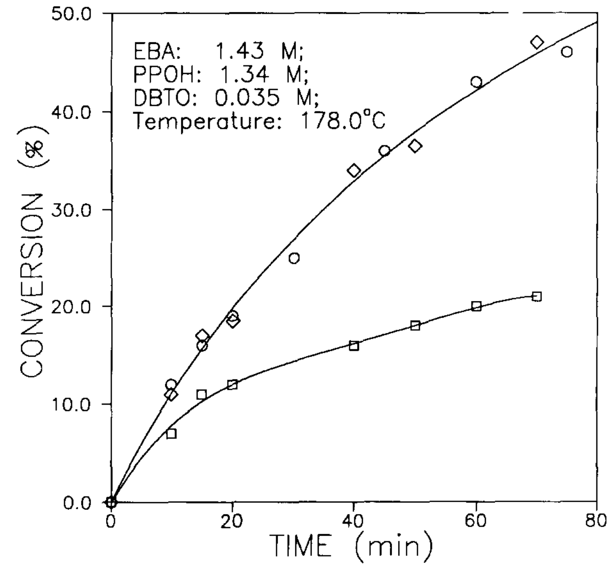


Figure 8 Effect of mechanical mixing on the overall reaction rate of the EBA/PPOH/DBTO system in the melt at 178°C. □, 0 rev min^{-1}; ◇, 64 rev min^{-1}; ○, 90 rev min^{-1}

64 and 90.5 rev min^{-1}, suggesting that a mixing speed of 64 rev min^{-1} is already high enough to homogenize the reacting system and to provoke efficient devolatilization of the product alcohols. In a screw extruder equipped with devolatilization facilities, the product alcohol removal is expected to be much more effective.

CONCLUSIONS

In this paper, we have presented the mechanism and kinetics of the transesterification of poly(ethylene-*co*-methyl acrylate), poly(ethylene-*co*-ethyl acrylate) and poly(ethylene-*co*-n-butyl acrylate) with 3-phenyl 1-propanol in 1,2,4-trichlorobenzene solution and in the melt. Dibutyltin dilaurate and dibutyltin oxide are the most efficient catalysts. These reactions are reversible in nature as confirmed in solution, and the equilibrium can be totally shifted to the product side in the melt. The reaction in solution and in the melt follows the same mechanism and kinetics. While the overall reaction proceeds much faster in the melt, the reaction rate constants in solution and in the melt are very close, despite the significant difference in viscosity and reactant concentrations. The close agreement between the respective rate constants obtained in both media has been attributed to the relatively low reaction rate compared with the diffusion rate of the model alcohol in the polymer melts. The reactivity of the alkyl acrylate decreases with the length of the alkyl group due to electrophilic and steric effects. The latter is supported by a higher activation energy observed for a longer acrylate. Mixing contributes to the overall reactivity by homogenizing reacting systems and by provoking effective devolatilization of the product alcohols. As the product alcohols can be removed more effectively in screw extruders, the reactivity potential of these ethylene and alkyl ester copolymers may be promising for reactive extrusion processes.

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