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Molten polyarylate–poly(butylene terephthalate) blends: kinetics and statistical analysis of the exchange reactions by ^{1}H n.m.r.

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The statistical and kinetic aspects of exchange reactions between a polyarylate and poly(butylene terephthalate) are considered. This theoretical approach enables us to calculate the average sequence length, the degree of randomness and the values of the kinetic parameters as a function of temperature and catalyst concentration from triad determination by n.m.r. spectroscopy.

(Keywords: poly(butylene terephthalate); polyarylate; kinetics)

INTRODUCTION

Interchange reactions in polycondensate blends offer an attractive alternative for the formation of new copolymers. Variation of the reaction parameters, such as temperature and reaction time, enables different products to be obtained, ranging from block to random copolymers. Knowledge of the dependence of the final product structure on the reaction parameters would permit materials with pre-determined properties to be obtained.

Characterization by n.m.r. of the structures resulting from interchange reaction has been reported in the literature. Yamadera and Murano[1] were pioneers in the evaluation of average sequence lengths and degree of randomness based on determination of three different types of triads. Devaux *et al.*[2] showed interchange reactions taking place in polycarbonate (PC)/poly(butylene terephthalate) (PBT) systems, and through the evolution of the corresponding dyads and triads, studied the kinetics assuming a direct transesterification mechanism.

Some other studies involving interchange reaction kinetics have been based on controlled degradation and further molecular weight measurements. Examples of such studies have been reported by Godard *et al.*[3] and Pilati *et al.*[4] for the system PC/poly(ethylene terephthalate) (PET), and by Devaux *et al.*[5] for a system composed of PC and a poly(aryl carboxylate). Similarly, Ramjit and Sedgwick[6] and Ramjit[7,8] studied the kinetics of the interchange reactions of poly(ethylene adipate)/poly(trimethylene adipate) by means of mass spectroscopy. Montaudo *et al.*[9–11] focused their kinetic analysis on different mixtures of polyesters with the help of mass spectroscopy, using n.m.r. as a complementary technique. Recently, different authors have used techniques as sophisticated as neutron scattering in order to follow the kinetics of these reactions, although the published results are not coincidental[12–15].

In previous publications by our group[16,17], the existence of interchange reactions in PBT/polyarylate (PAr) systems was evidenced by means of n.m.r. and *FT*i.r. Thus, using model compounds we were able to identify all the structures formed as a consequence of the interchange reactions.

In the present article we report on the microstructure of this system by ^{1}H n.m.r. On the basis of the number of triads, we have calculated the degree of randomness and the average sequence lengths, as well as the effect of temperature and catalyst concentration on these parameters.

THEORY

Statistical study of the reaction

The analysis is based upon the measurements of the ^{1}H n.m.r. signal intensities, using n.m.r. triad data. These data have led us to calculate the degree of randomness (B) and the average sequence lengths (X). However, it is worthwhile pointing out that this procedure is not strictly correct because these parameters have been defined on the basis of the hypothesis of infinite molecular weights. Furthermore, the peculiar properties of B refer to a pure copolymer and not to a mixture of unconverted homopolymers and copolymer.

In this paper we are only considering copolycondensates resulting from an exchange reaction between two linear polycondensates, disregarding polycondensate chain ends in the calculation because of their high degree of polymerization.

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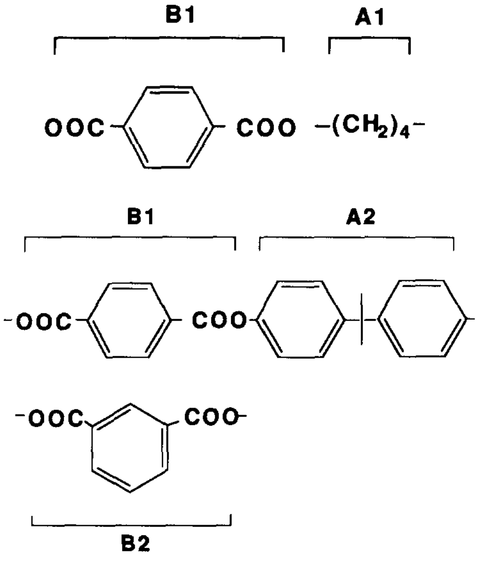
If we represent the repeat units of our system by:



the initial triads will be:

$$A_1\text{–}B_1\text{–}A_1 \qquad A_2\text{–}B_1\text{–}A_2 \qquad A_2\text{–}B_2\text{–}A_2$$

As a consequence of the transesterification reaction, the following structures will be formed:

$$A_1\text{–}B_1\text{–}A_2 \qquad A_1\text{–}B_2\text{–}A_2 \qquad A_1\text{–}B_2\text{–}A_1$$

We will focus the analysis on the triads centred on B_1 because there is no reason to calculate sequence lengths of $-A_2-B_2-$, due to the random copolymer nature of PAr.

Following a method similar to that of Yamadera and Murano[1] and Devaux *et al.*[2] it is possible to define B_{B1} (degree of randomness centred on B_1) as:

$$B_{B1}=p_{A1B1A2}+p_{A2B1A1}=\frac{f_{A1B1A2}}{2}\left(\sum_{i=1}^{2}\frac{1}{f_{Ai}}\right) \tag{1}$$

where p_{A1B1A2} is the probability for a triad centred on B_1 and beginning with A_1 to end with A_2, p_{A2B1A1} is the probability for a triad centred on B_1 and beginning with A_2 to end with A_1, f_{Ai} is the molar fraction of A_i relative to total concentration of A, and f_{A1B1A2} is triad molar fraction referred to the total number of triads around B_1. B_{B1} can assume values between 0 and 2. $B_{B1}=0$ corresponds to the case where no or very little transesterification has occurred. $B_{B1}=1$ indicates that transesterification has progressed to such a point that a copolymer is produced with a random distribution of A_1 and A_2 units around B_1. Values of B_{B1} between 1 and 2 indicate a tendency for A_1 and A_2 to alternate around B_1.

Finally, the average sequence length of A_1B_1, assuming a Bernoullian distribution, can be written as:

$$\bar{X}_{A1B1}=\frac{f_{A1B1A1}+\frac{1}{2}f_{A1B1A2}}{\frac{1}{2}f_{A1B1A2}} \tag{2}$$

Kinetic study

The mechanism of a direct transesterification between a homopolycondensate and a copolycondensate having one structural unit partly in common can be written as:

$$\begin{array}{llll}
 & -A_1-B_1-A_1- \;+ & -A_2-B^*-A_2- & \\
i{:} & a & b & \\
f{:} & (a-x) & (b-x) & \\
 & \xleftrightarrow{k_1,k_{-1}} & -A_1-B_1-A_2- \;+ & -A_1-B^*-A_2- \\
 & & (x) & (x)
\end{array}$$

where i represents the initial time, f the equilibrium time, a the initial F_{A1} molar fraction, b the initial F_{A2} molar fraction, and x the molar fraction of triads centred on B_1 or B^* and beginning with A_1 to end with A_2. B^* represents B_1 or B_2 in the ratio found in the copolycondensate at the initial time.

Assuming, as did Devaux *et al.*[2] and Ramjit and Sedgwick[6], a second-order reversible reaction, we can write:

$$\frac{dx}{dt}=k_1(a-x)(b-x)-k_{-1}(x)^2 \tag{3}$$

Since the copolyester is random at equilibrium, we have $x_e=ab$, and thus equation (3) will be written as:

$$\frac{dx}{dt}=k_1(x_e-x) \tag{4}$$

Defining the transesterification ratio $r=x/a$ and integrating equation (4), we obtain the kinetic expression:

$$\ln\left[\frac{b}{(b-r)}\right]=k_1t \tag{5}$$

This expression permits the determination of the transesterification rate constant (k_1) from measurements of the ratio r.

EXPERIMENTAL

The two polymers used in this study (PAr and PBT) were supplied by Union Carbide and Polysciences, respectively. PAr is a copolyester of bisphenol A and an equimolar mixture of ter and isophthalic acids. Their molecular characteristics and blend preparation have been described elsewhere[16]. The catalyst employed was tetra-n-butyl titanate (Aldrich), a catalyst widely used in the polymerization of PBT.

A Mini Max moulder (CSI) was used to run the reaction. Reaction temperatures were 260, 270 and 280°C, and reaction times ranged between 20 and 540 min. All mixtures contained 50/50 (w/w) PBT/PAr with a catalyst concentration of 0.005%. This concentration corresponds to the residual catalyst from PBT polymerization after polymer purification. Additional catalyst was added to some of the samples in order to increase its concentration up to 0.1% and 0.2%. Atomic absorption spectrophotometry was used to measure catalyst concentration.

N.m.r. spectra were registered in a Varian VXR 300 spectrometer in a 50/50 mixture of deuterated trifluoroacetic acid and deuterated chloroform; tetramethylsilane (TMS) was used as internal reference. ^1H n.m.r. (300 MHz) spectra were registered in 5 mm i.d. tubes in 10% w/v solutions with a spectral width of 4000 Hz, flip angle 90° and acquisition time 3.7 s; 16 K data points were used for Fourier transform.

RESULTS AND DISCUSSION

Statistical analysis of the structures

From the previously identified[17] ^{1}H n.m.r. signals, it is possible to calculate the relation of triads in the reaction mixture. *Table 1* shows the fraction of triads centred on B_1 for a mixture of PBT/PAr (50/50) with a residual catalyst concentration of 1.16×10^{-6} mol g^{-1} at 270°C, depending on the reaction time. As can be seen, there is a significant increase in the interchange units and a decrease in the units corresponding to the initial homopolymers.

Figures 1 and *2* show the variation of the degree of randomness and the average sequence length with the reaction time for the three temperatures investigated. It can be seen that at 280°C the values of B become almost 1, indicative of the formation of a random copolymer. At 260 and 270°C, the reaction tends to the formation of a random copolymer, but this occurs beyond the experimental time range. These results, in apparent contradiction to others reported in the literature, can be explained by the fact that in our study the catalyst concentration was low, as the homopolymers used had been purified by solution/precipitation. The presence of a very low catalyst concentration results in a longer reaction time being required to reach the structure of a random copolymer.

Table 1 Fraction of triads centred on B_1 for PBT/PAr at 270°C

Time (min)	f_{A1B1A1}	f_{A2B1A2}	f_{A1B1A2}
0	0.770	0.230	0.000
30	0.738	0.199	0.062
50	0.724	0.193	0.076
90	0.715	0.175	0.110
130	0.691	0.177	0.132
240	0.610	0.152	0.237
300	0.583	0.151	0.266
420	0.554	0.140	0.306
Statistical copolymer	0.384	0.144	0.471

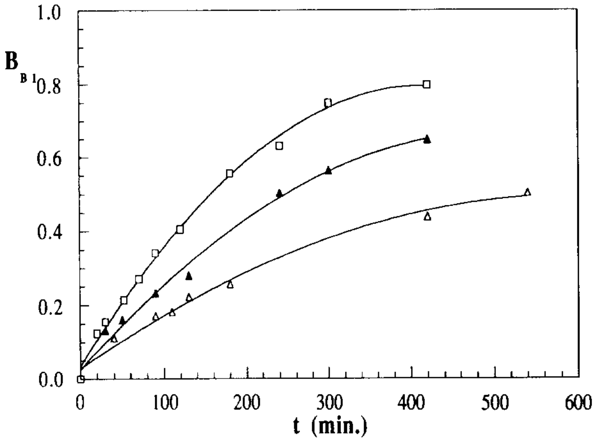


Figure 1 Degree of randomness (B) *versus* reaction time: △, 260°C; ▲, 270°C; □, 280°C

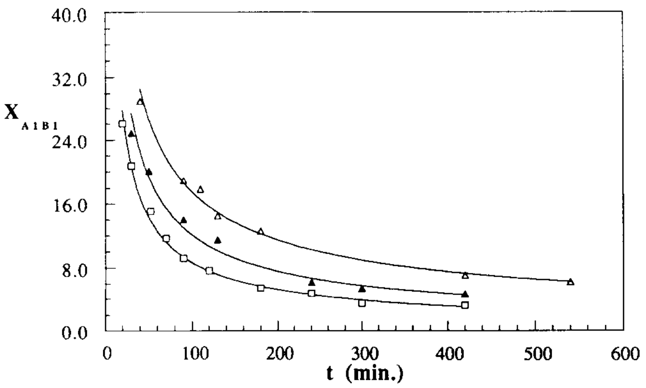


Figure 2 Average sequence length *versus* reaction time: △, 260°C; ▲, 270°C; □, 280°C

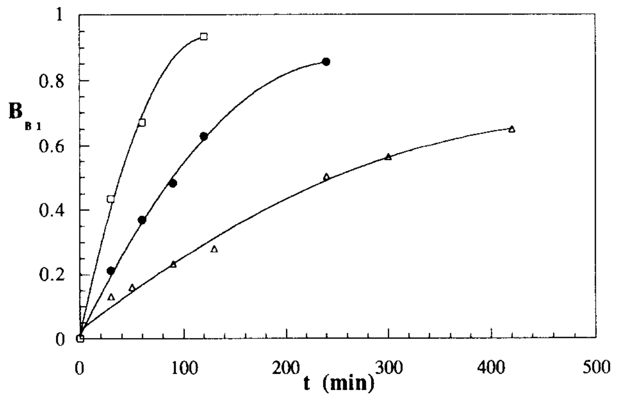


Figure 3 Degree of randomness (B) *versus* reaction time at 270°C. Catalyst concentration (mol g^{-1}): △, 1.16×10^{-6}; ●, 2.28×10^{-5}; □, 4.14×10^{-5}

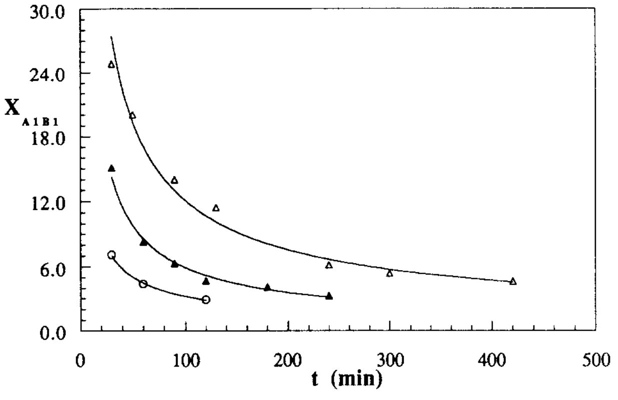


Figure 4 Average sequence length (X) *versus* reaction time at 270°C. Catalyst concentration (mol g^{-1}): △, 1.16×10^{-6}; ▲, 2.28×10^{-5}; ○, 4.14×10^{-5}

In order to study the influence of the catalyst on the evolution of the interchange reaction, different amounts of catalyst were added to the blends.

Figures 3 and *4* show the variation of B and X as a function of the reaction time and catalyst concentration at 270°C. The effect of the catalyst on these parameters is clear. Thus, acceleration of the process reduces the time required to reach the structure of a random copolymer.

Reaction kinetics

Taking into account all the prior considerations, and assuming the mechanism of the reaction to be direct transesterification, we can use equation (5) to study the kinetics of the reaction.

In our case, a and b values are 0.620 and 0.380, respectively. The values of x can be obtained directly from the integration of the corresponding signals from ^{1}H n.m.r. spectra. The reaction constant k_1 is obtained from the slope of a representation of $\ln(b/b-r)$ *versus* reaction time (t). As shown in *Figure 5*, the theoretical expression (6) is closely followed by these systems, and therefore the kinetic hypothesis, as second-order reversible reaction and a random distribution of the units at equilibrium, can be considered correct.

In the same way we investigated the influence of the catalyst at three temperatures. *Figure 6* shows the reaction kinetics at 270°C and three different catalyst concentrations. As can be seen, there is clear evidence of the increase of the slope with the concentration of catalyst, which confirms the ability of tetra-n-butyl titanate to catalyse a transesterification reaction.

Table 2 reports the reaction constants obtained from various PAr/PBT mixtures at three temperatures and catalyst concentrations. From the representation of $\ln k_1$ *versus* $1/T$ for those systems with a residual content of catalyst ($1.16\times10^{-6}\,\mathrm{mol\,g^{-1}}$) and using an Arrhenius type equation, we have obtained an expression for k_1 as:

$$k_1(\mathrm{min^{-1}}) = 1.443\times10^{13}\exp\left(\frac{-39\,105}{RT}\right) \qquad (6)$$

A logarithmic plot of the rate constant k_1 as a function of catalyst concentration yields a straight line, which permits the determination of the dependence of the rate constant on catalyst concentration. However, it must be pointed out that in doing this calculation, we have considered the same reactivity for the residual catalyst and for the additional catalyst. This assumption should be made with caution, as it has not been proved either correct or false. Therefore, we assume that the activation energy takes the same value for both cases.

Table 2 Reaction constants as a function of temperature and of catalyst concentration for PBT/PAr (50/50) mixtures

Catalyst concentration (10^{-5} mol g^{-1})^a	T (°C)	k_1 (10^{-3} min^{-1})
0.116	260	1.12
2.47	260	5.67
4.47	260	9.21
0.116	270	2.49
2.28	270	8.10
4.44	270	17.48
0.116	280	4.30
2.28	280	19.28
4.41	280	25.93

^{a} Mole catalyst per gram of polymer

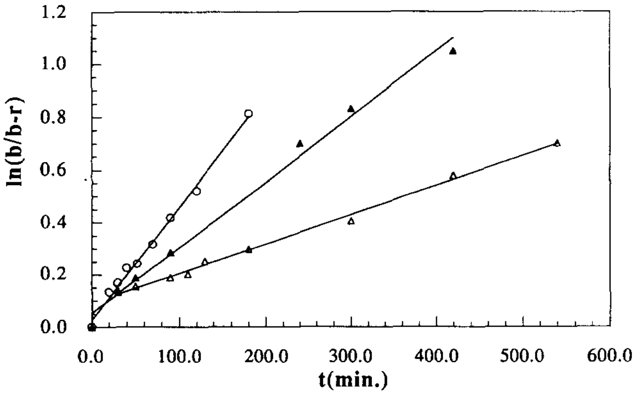


Figure 5 Transesterification kinetics of PBT/PAr in a 50/50 blend: △, 260°C; ▲, 270°C; ○, 280°C

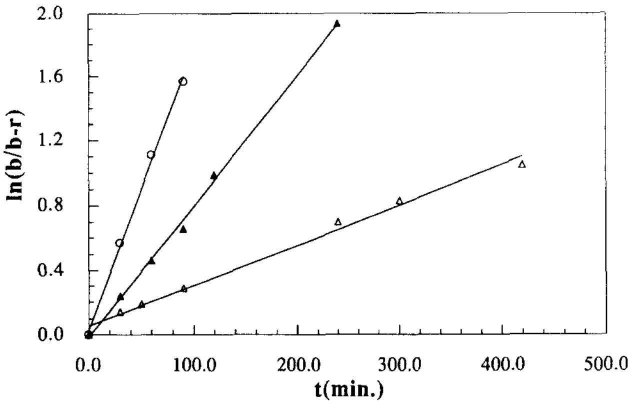


Figure 6 Transesterification kinetics of PBT/PAr in a 50/50 blend at 270°C. Catalyst concentration (mol g^{-1}): △, 1.16×10^{-6}; ▲, 2.28×10^{-5}; ○, 4.14×10^{-5}

The following expression was finally obtained for the transesterification rate constant k_1:

$$k_1(\mathrm{min^{-1}}) = 2.004\times10^{16}[\mathrm{Ti}]^{0.53}\exp\left(\frac{-39\,105}{RT}\right) \qquad (7)$$

in which the concentration of the catalyst, [Ti], is given in moles per gram and the activation energy in calories per mole. These values, except the order of reaction with respect to catalyst concentration, are comparable to those obtained for similar systems described in literature[2,3,5].

CONCLUSIONS

The interchange reaction taking place in PBT/PAr blends was studied. It has been shown that this reaction leads to the formation of a random copolymer. However, without additional catalyst, the time required for a random distribution is very long compared to other systems described in the literature.

The behaviour of the system is in accordance with the theoretical mechanism of a direct transesterification. The values obtained for the reaction constant and the activation energies are comparable to those described in the literature for similar systems. Nevertheless, the value of the reaction order with respect to Ti concentration is different from those of the cited systems.

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