polymer papers

Interpretation of neutron scattering results during transesterification reactions

H. C. Benoît
Institut Charles Sadron (CRM–EAHP; CNRS–ULP), 6 rue Boussingault, 67083 Strasbourg Cedex, France

and E. W. Fischer
Max-Planck-Institut für Polymerforschung, PO Box 3148, 6500 Mainz, FRG

and H. G. Zachmann
Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstrasse 45, 2000 Hamburg, FRG
(Received 23 May 1988; accepted 18 July 1988)

We present equations describing the evolution of intensity scattered by a mixture of two homopolyesters in a neutron experiment when there is a transesterification reaction and the contrast between the two types of polyester is sufficient. This theory predicts the evolution of the signal as a function of the progress of the reaction and allows the determination of the velocity constant K of the reaction. It also predicts that, at the beginning of the reaction, as well as at its end, the graph, $i^{-1}(q)$ as a function of q^2 should be a straight line in the intermediate q range ($1/R_g < q < 1/b$), where R_g is the radius of gyration and b is the length of the statistical segment. In addition it is shown that this scattering law is valid for any $q < 1/b$ if the block lengths obey the most probable distribution.

(Keywords: neutron scattering; transesterification)

INTRODUCTION

If a mixture of two compatible polyesters A and B is heated, copolyesters are rapidly obtained, which means that scission and recombination reactions take place in the system. This phenomenon, which is called transesterification, is well known by industrial chemists and has been studied by the classical analytical methods available for the characterization of composition and sequence length of copolymers and copolycondensates. Recently, small angle neutron scattering has been used to study this problem[1–5]. It is easy to show qualitatively why the neutron scattering technique is well adapted to this problem. If one has a mixture of two homopolyesters, one deuterated and the other not, they will give an intense signal in a neutron scattering experiment which can be interpreted by the classical de Gennes[6] formula. This experiment is analogous to the first experiments made on mixtures of deuterated and ordinary polystyrenes in the early days of the neutron scattering technique. Now let us assume that we heat the system in order for transesterification to take place. The system becomes a mixture of copolyesters. The contrast diminishes because all the molecules become similar and the scattered intensity will disappear almost completely if the reaction goes to completion[7]. This technique is probably the best available method because it is very sensitive, especially at the beginning of the reaction.

In this paper we give a theoretical treatment of the problem in order to be able to propose a quantitative interpretation of the experimental results and a precise determination of the kinetic parameters of the reaction. We use as a first example a mixture of a deuterated and an ordinary polyester of the same nature, differing only in their contrast factors. In this case we give a general expression for the intensity $I(q,t)$ scattered by the sample at time t, where q is the modulus of the scattering vector $(4\pi/\lambda)\sin\frac{1}{2}\theta$, with λ the wavelength of the incident beam, θ the angle between the incident and the scattered beams and t the time elapsed after the beginning of the transesterification reaction.

We first limit our analysis to the behaviour at large q, showing how it is possible to relate the experimental feature of the scattering diagram to the kinetics of the reaction. In the last part of the paper we explore the information one can obtain from the complete $I(q)$ curve and generalize our results to polyesters of different nature.

CALCULATION OF INTENSITY SCATTERED AT LARGE q

Hypotheses and notation

Since we assume that the two polyesters differ only in their coherent scattering length (we assume that the incoherent scattering has been subtracted), they can be considered to have the same statistical length per monomeric unit, which we will call b. We also assume that the two monomeric units, even if they do not have the same weight, occupy the same volume. This hypothesis is not indispensable but simplifies the equations. Since it is difficult to obtain monodisperse polyesters, we shall take into account the polydispersity of the initial polyesters.

0032-3861/89/030379-07$03.00

We will denote the total number of monomeric units D and H in the sample by N_D and N_H and their total number by N_T. The number fraction x of units D is defined as

$$x=\frac{N_D}{N_H+N_D}=\frac{N_D}{N_T}, \quad 1-x=\frac{N_H}{N_H+N_D}=\frac{N_H}{N_T} \tag{1}$$

Following our hypothesis, x is also the volume fraction of the D units in the sample.

The total number of chains D and H will be called ν_D and ν_H respectively. This allows us to define the number average degree of polycondensation n_D and n_H of these polyesters by the relations

$$n_D^0=\frac{N_D}{\nu_D}, \quad n_H^0=\frac{N_H}{\nu_H} \tag{2}$$

The number average degree of polycondensation of the total sample, n_T, obtained without differentiating between monomers D and H, will be useful later and is defined as

$$\frac{1}{n_T^0}=\frac{x}{n_D^0}+\frac{1-x}{n_H^0} \tag{3}$$

We will assume that the chains are Gaussian, which means that for a monodisperse system their structure factor is given by the Debye expression[8]

$$P(q)=\frac{2}{(\lambda n)^2}[\lambda n-1+\exp(-\lambda n)] \tag{4}$$

where $\lambda=q^2b^2/6$.

The scattered intensity will be characterized by $i(q)$, which is defined as

$$i(q)=\frac{I(q)}{N_T}\frac{1}{(a_H-a_D)^2} \tag{5}$$

where a_D and a_H are the coherent scattering lengths of the D and H monomers, respectively.

Initial scattering

With this notation and if the polyesters are monodisperse, one can write, according to de Gennes[6]

$$i^{-1}(q)=\frac{1}{xn_DP_D(q)}+\frac{1}{(1-x)n_HP_H(q)}-2\chi \tag{6}$$

where χ is the interaction parameter between D and H monomeric units. Since the polyesters are usually polydisperse, one has to use the generalization of this equation for polydisperse systems and write

$$i^{-1}(q)=\frac{1}{xn_{D_w}\langle P_D(q)\rangle}+\frac{1}{(1-x)n_{H_w}\langle P_H(q)\rangle}-2\chi \tag{7}$$

defining $\langle P(q)\rangle$ by the equation

$$\langle P(q)\rangle=\frac{1}{\sum \nu_i n_i^2}\sum_i \nu_i n_i^2 P_i(q) \tag{8}$$

Using the procedure proposed by Benoît[9] a long time ago one can replace $\langle P(q)\rangle$ by its asymptotic expression, obtaining from equations (4) and (7):

$$\frac{1}{i(q)}=\frac{q^2b^2}{12x(1-x)}+\frac{1}{2}\left[\frac{1}{xn_D}+\frac{1}{(1-x)n_H}\right]-2\chi \tag{9}$$

This equation can be written in a slightly different form in order to introduce the total number average molecular weight of the sample as defined in equation (3):

$$\frac{1}{i(q)}=\frac{q^2b^2}{12x(1-x)}+\frac{1}{2x(1-x)}\left(\frac{1}{n_D^0}+\frac{1}{n_H^0}-\frac{1}{n_T^0}\right)-2\chi \tag{10}$$

Note that the expression in parenthesis is always positive. This expression for $i(q)$ can be used in what is called the intermediate range, i.e. the range of q which satisfies the inequalities

$$\frac{1}{R}<q<\frac{1}{b} \tag{11}$$

where R is the radius of gyration of the smallest polyester. If these macromolecules are sufficiently large this is a very convenient range for the neutron scattering technique. The experiments therefore require large values of n_D^0 and n_H^0. They also require the use of values of λn which are not too far from $\lambda n=0.5$ since otherwise the signal would be too small to be measured easily.

Scattering after the start of the reaction

As soon as the reaction has begun the system becomes very complex since it contains deuterated and hydrogenated homopolyesters as well as copolycondensates of various compositions and numbers of blocks. The problem seems difficult but we will see that the result is very simple in the intermediate range.

We start with the generalization of the de Gennes formula to copolymers[10–12], which can be written as

$$\frac{1}{i(q)}=\frac{n_{T_w}\langle P_T(q)\rangle}{x(1-x)(n_{H_w}\langle P_H\rangle n_{D_w}\langle P_D\rangle-n_{DH_w}^2\langle P_{DH}^2\rangle}-2\chi \tag{12}$$

In this formula n_{T_w}, n_{D_w} and n_{H_w} are the weight average degrees of polycondensation of the whole polymer, its deuterated part and its 'ordinary' part, respectively. The functions $\langle P_{T_w}\rangle$, $\langle P_{D_w}\rangle$ and $\langle P_{H_w}\rangle$ are average structure factors, as defined in equation (8) for the whole polymer, its deuterated part and its ordinary part, respectively. The quantity P_{DH_w} is a cross term characterizing the interference between the D and H part of the same molecule; it is defined for a monodisperse system by the equation

$$n_H n_D P_{HD}=\langle\sum_{i_H}\sum_{j_D}\exp(-iqr_{i_H i_D})\rangle \tag{13}$$

and for a polydisperse by the relation

$$\langle P_{DH}(q)\rangle=\frac{1}{\sum \nu_i n_{Hi} n_{Di}}\sum \nu_i n_{i_H} n_{iD} P_{iDH}(q) \tag{14}$$

where ν_i is the number of molecules having n_{iH} monomers H, n_{iD} monomers D and a cross structure factor $P_{iDH}(q)$.

These formulae are also valid for mixtures containing homopolycondensates. When all macromolecules are homopolyesters, the cross term is zero and one recovers formula (7). To write the value of this expression in the intermediate range we have to know the asymptotic expansion of all the terms of formula (12). It has been shown[13] that the cross term does not contribute to this expansion since it decreases faster than the other terms when q increases. This simplifies the calculations and, after elementary algebra, one obtains for the intermediate q range in the case of block copolymers

$$\frac{1}{i(q)}=\frac{q^2b^2}{12x(1-x)}+\frac{1}{2x(1-x)}\left[\frac{1}{n_D(t)}+\frac{1}{n_H(t)}-\frac{1}{n_T^0}\right]-2\chi \quad (15)$$

This equation looks similar to equation (10), which describes the scattering by a mixture of homopolymers, but now $n_D(t)$ and $n_H(t)$ are the time dependent number average degrees of polymerization of the sequences D and H, respectively; n_T^0 is the number average degree of polymerization of the block copolymer molecules, which, according to experimental results, is assumed to remain constant.

This result is very simple and will allow the prediction of the shape expected from the experimental curves. If we plot $i^{-1}(q)$ as a function of q^2 using equation (15) we obtain a figure similar to *Figure 1*. The straight lines in *Figure 1* are the curves which have to represent the experimental data. We shall show later that the limit $1<qR$ is, usually, much less severe than it looks from the inequality. Two things should be noted about the curves. First, the slope of these curves does not depend on time or on the yield of the transesterification reaction since it depends only on the composition x and on the value of the statistical element b. From our hypothesis the Gaussian behaviour is not affected by the reaction and this slope should not change even when the system has reached its final state: a statistical copolymer. Second, the only parameter which does depend on time is the intercept, i.e. the ordinate z of the intersection of the straight lines with the y-axis. This quantity is given by

$$z=\frac{1}{2x(1-x)}\left[\frac{1}{n_D(t)}+\frac{1}{n_H(t)}-\frac{1}{n_T^0}\right]-2\chi \quad (15')$$

If the total molecular weight does not change during the reaction, z is an increasing function and the scattered intensity a decreasing function of time. In fact the situation is very favourable since z is perhaps the most readily available experimental quantity. The precision on it is certainly larger than the precision on the zero angle scattering and on the radius of gyration.

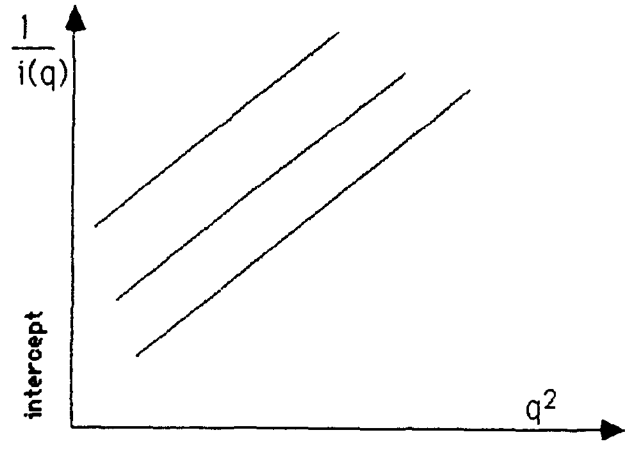
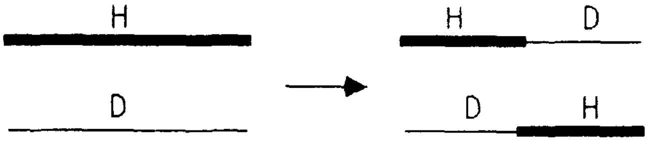


Figure 1

Relation between intercept and number of scissions

Since the experiment shows that the number average molecular weight of the sample does not change, the transesterification reaction must proceed with an equal number of chain scissions and chain recombinations. One can therefore assume a model in which one D chain and one H chain are broken to form two HD chains, following *Scheme 1*, where the light and heavy lines represent the D and H sequences. The scissions and recombinations which have been considered here are not the only reactions taking place in the system. What we have described is the reaction

Scheme 1



$$R^1H-HR^2+R^3D-DR^4 \rightleftharpoons R^1H-DR^3+R^2H-DR^4$$

but other reactions like

$$R^1H-HR^2+R^3H-HR^4 \rightleftharpoons R^1H-HR^3+R^2H-HR^4$$

or their equivalent with D monomers are also possible. They do not introduce any change in the number of sequences D and H and therefore have no influence on the intermediate scattering. In this sense they are not efficient and will not be considered here. If we call w_0 the probability for an interchange reaction, the probability for an efficient reaction will be $2w_0x(1-x)$ and will be the only one taken into consideration. (Remember that the probabilities for a D–D, D–D reaction and a H–H, H–H reaction to occur are, respectively, x^2 and $(1-x)^2$ times w_0.)

From *Scheme 1* is it evident that every efficient scission and recombination increases by one unit the number of D blocks and of H blocks. This means that, after S scissions and recombinations, the numbers of blocks D and H, which were originally ν_D and ν_H, become ν_D+S and ν_H+S. Their number average degree of polymerization is

$$n_D(t)=\frac{N_D}{\nu_D+S}, \qquad n_H(t)=\frac{N_H}{\nu_H+S} \quad (16)$$

From these values we can immediately evaluate (with the help of equation (15)) the quantity z, the intercept of the asymptote of the experimental curve with the y-axis, obtaining:

$$z=\frac{1}{2x(1-x)}\left(\frac{1}{n_H^0}+\frac{S}{N_H}+\frac{1}{n_D^0}+\frac{S}{N_D}-\frac{1}{n_T^0}\right)-2\chi \quad (17)$$

Calling z_0 the value of z at time $t=0$ (before the beginning of the reaction) one obtains:

$$z(t)=z_0+\frac{1}{2x^2(1-x)^2}\frac{S(t)}{N_{\mathrm{T}}} \tag{18}$$

This formula is strikingly simple. The experimental quantity $z(t)-z_0$ depends only (after normalization of the absolute intensity) on the quantities x and N_{T}, which must be known from the preparation of the sample. They depend neither on the interaction parameter χ nor on the molecular weights of the starting polyesters, which quantities are difficult to measure. The only limitation is that we have to assume that the blocks are Gaussian. This hypothesis could be incorrect at the end of the reaction when the number of monomeric units in each sequence becomes very small.

REACTION KINETICS

General considerations

It has been shown that upon measuring the intensity scattered by a mixture of deuterated and undeuterated polyesters during a transesterification reaction, one obtains what has been called the number of efficient scissions $S(t)$. This number is not the total number of scissions but only the number of scissions modifying the number of sequences H–H and D–D following the reaction which can be symbolized by the equation

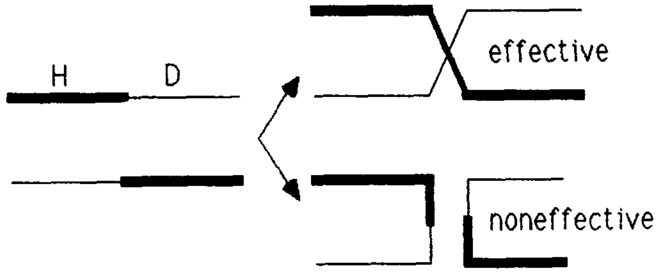
$$\text{H–H}+\text{D–D}\rightleftharpoons 2\text{H–D} \tag{19}$$

If we assume that the molecular weights of the initial polyesters are large, neglecting end effects, the number of D–D and H–H bonds in the initial mixture is equal to the number of D and H monomers N_{D} and N_{H}. (In fact we could introduce a correction by writing $N_{\mathrm{DD}}=N_{\mathrm{D}}-\nu_{\mathrm{D}}$ and $N_{\mathrm{HH}}=N_{\mathrm{H}}-\nu_{\mathrm{H}}$, but this correction can be neglected in most cases.) Let us call $S_{\mathrm{D}}(t)$, $S_{\mathrm{H}}(t)$ and $S_{\mathrm{HD}}(t)$ the number of D–D, H–H and H–D bonds at time t. The rate of reaction, going from left to right, is given by

$$\frac{\mathrm{d}S_{\mathrm{HD}}(t)}{\mathrm{d}t}=k_{-}S_{\mathrm{H}}(t)S_{\mathrm{D}}(t) \tag{20}$$

Going from right to left one has to take into account that only half of the reactions lead to a change in the number of sequences. This is demonstrated in *Scheme 2*. Therefore,

Scheme 2



the backwards reaction reads as

$$-\frac{\mathrm{d}S_{\mathrm{HD}}(t)}{\mathrm{d}t}=k_{-}\left[\frac{1}{2}S_{\mathrm{HD}}(t)\right]^2 \tag{20'}$$

Since the only differences are due to isotopic effects we can write

$$k_{+}=k_{-}=k$$

and the overall rate of change of S_{HD} obeys the equation

$$\frac{\mathrm{d}S_{\mathrm{HD}}(t)}{\mathrm{d}t}=k\{[S_{\mathrm{H}}(t)S_{\mathrm{D}}(t)]-\tfrac{1}{4}[S_{\mathrm{HD}}(t)]^2\} \tag{21}$$

This gives for the equilibrium situation

$$[S_{\mathrm{HD}}(t)]^2=4S_{\mathrm{H}}(t)S_{\mathrm{D}}(t) \tag{22}$$

Taking into account the initial conditions and using the number of efficient scissions $S(t)$ defined above one obtains at any time:

$$\begin{aligned}S_{\mathrm{D}}(t)&=N_{\mathrm{T}}x-S(t)\\ S_{\mathrm{H}}(t)&=N_{\mathrm{T}}(1-x)-S(t)\\ S_{\mathrm{HD}}(t)&=2S(t)\end{aligned} \tag{23}$$

The equilibrium distribution is given by equation (22) and by the condition that

$$S_{\mathrm{D}}+S_{\mathrm{H}}+S_{\mathrm{HD}}=N_{\mathrm{T}}$$

giving directly

$$\begin{aligned}S_{\mathrm{D}}&=N_{\mathrm{T}}x^2\\ S_{\mathrm{H}}&=N_{\mathrm{T}}(1-x)^2\\ S&=N_{\mathrm{T}}x(1-x)\end{aligned} \tag{24}$$

Knowing this equilibrium distribution, one can write the expression for the scattered neutrons for $t=\infty$, obtaining from equation (17)

$$\frac{1}{i(q)}=\frac{q^2b^2}{12x(1-x)}+\frac{1}{2x(1-x)}\left(\frac{1}{n_{\mathrm{D}}^0}+\frac{1}{n_{\mathrm{H}}^0}-\frac{1}{n_{\mathrm{T}}^0}+1\right)-2\chi$$

or, neglecting $1/n_{\mathrm{T}}^0$, $1/n_{\mathrm{D}}^0$ and $1/n_{\mathrm{H}}^0$, which are small compared to unity

$$\frac{1}{i(q)}=\frac{q^2b^2}{12x(1-x)}+\frac{1}{2}\left(\frac{1}{x}+\frac{1}{1-x}\right)-2\chi \tag{25}$$

This corresponds to a very small intensity. More precisely, using equation (9) one obtains the same scattered intensity $i(0)$ (at $q=0$) on a mixture of deuterated and ordinary monomers in the proportion x, $(1-x)$, $(n_{\mathrm{H}}=n_{\mathrm{D}}=1)$.

The quantity S(t)

The differential equation can be solved since one can eliminate $S_{\mathrm{D}}(t)$ and $S_{\mathrm{H}}(t)$ using equation (23), obtaining

$$\frac{\mathrm{d}S}{\mathrm{d}t}=\frac{k}{2}\{[N_{\mathrm{T}}x-S(t)][N_{\mathrm{T}}(1-x)-S(t)]-S^2(t)\} \tag{26}$$

and from it

$$S(t) = N_T x(1-x)[1-\exp(-\tfrac{1}{2}kN_T t)] \tag{27}$$

This equation shows that, starting from zero, $S(t)$ reaches its equilibrium value exponentially with a relaxation time $\tau = 2/kN_T$. Inserting this value of $S(t)$ into the expression for $z - z_0$ (equation (18)) one obtains

$$z - z_0 = \frac{1}{2x(1-x)}[1-\exp(-t/\tau)] \tag{28}$$

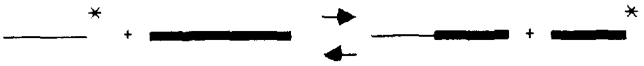
This value inserted in equation (15) gives the final result

$$\frac{1}{i(q)} = \frac{q^2b^2}{12x(1-x)} + \frac{1}{2x(1-x)}\left[\frac{1}{n_D} + \frac{1}{n_H} - \frac{1}{n_T} + 1 - \exp(-t/\tau)\right] - 2\chi \tag{29}$$

which shows clearly how $i(q)$ varies with time and allows the velocity constant τ to be determined from the experimental values. Note that a plot of $x(1-x)/i(q)$ yields a master curve independent of the starting concentration if $\chi \approx 0$. This has been established experimentally[21].

Another model for transesterification

One can ask the question whether there are other models for this transesterification reaction. We did not find an answer to this question in the literature and we have considered the following model involving the chain ends. We assume that the chain ends are active and can react on a polyester molecule following the model



The active end breaks a chain and adds itself onto one of the sequences, the activity being transferred to the other sequence. As in the other model, if the active chain is H (or D) and the broken chain is D (or H) blockcopolyesters are formed and, therefore, transesterification occurs. These reactions can be schematized as follows:

$$\begin{aligned} D_e + H\text{–}H &\rightleftharpoons D\text{–}H + H_e \\ H_e + D\text{–}D &\rightleftharpoons H\text{–}D + D_e \end{aligned} \tag{30}$$

where D_e and H_e denote the deuterated and non-deuterated terminal monomers, respectively. By adding these two equations we obtain

$$H\text{–}H + D\text{–}D \rightleftharpoons 2H\text{–}D \tag{31}$$

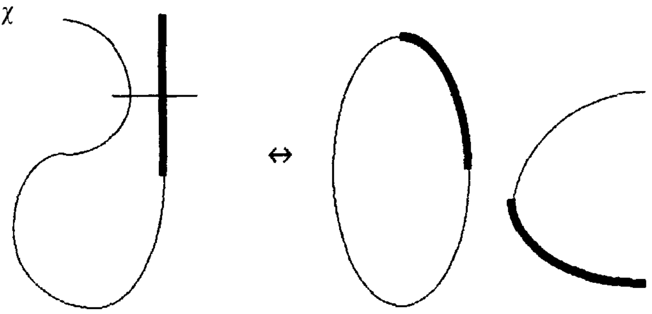
which is the same as equation (19). This model leads to the same equations and therefore to the same results. Nothing is changed in the analysis except the significance of the rate constant, which will be called k'. From equation (30) one sees clearly that k' depends on the concentration of the chain ends. In this scheme this concentration is stationary, and this is the reason why it does not figure in the result but k' depends on it. Increasing the length of the chains decreases the concentration of the species D_e and H_e; this makes the reaction slower. A study of the effect of molecular weight on the kinetics of the reaction could allow a choice between these two models.

Influence of cyclization

As in polycondensation reactions the formation of cyclic macromolecules cannot be excluded in transesterification reactions. In all the preceding discussions we did not take the existence or formation of cycles into account so it is important to know if they affect our conclusions.

Cycles can be obtained by the mechanisms we have discussed; *Scheme 3* explains how this is possible in the first case and it is evident that a similar scheme could be drawn for the second. Note that cycles are formed as well by 'inefficient reactions' as by 'efficient' ones. Each time a cycle is formed a new sequence is also formed, which means that the cycles do not affect the relation between the number of scissions and the length of the sequences. Two things are modified: first, the number of chains ($\nu_D + \nu_H$ and n_T will no longer stay constant); and second, the structure factor of a cyclic chain is not given by the Debye[8] formula but by the Casassa[14] equation, which is slightly different.

Scheme 3



Concerning the first point, remember that in homopolyesters at the beginning of the reaction there are also cyclic molecules and that, during the exchange reaction, their number should not change if this reaction is carried out at the polycondensation temperature. If the transesterification occurs at another temperature there will be a new equilibrium between cycles and linear molecules which could affect the number of chains. This change is difficult to detect by size exclusion chromatography since the hydrodynamical volumes of cycles and linear molecules are not identical[15]. Anyway, as long as the number of scissions is sufficiently large, this correction is small. The second effect could be more important. Our analysis is based on the second term of the expansion of the structure factor as a function of q^{-1} and it is known that this term is different for rings. Fortunately it has been shown by Hadziioannou and Benoît[16] that, as soon as the number of sequences is larger than ≈ 10, there is no detectable difference between the scattering of a linear chain and that of a ring. This discussion shows that the presence of rings in the sample should not affect dangerously the method of interpretation proposed here.

COMPLETE SCATTERING CURVE

The only quantities which have been discussed up to now have been in what we have called the intermediate range.

This was very convenient since the only average which had to be taken into account was the number average degree of polymerization, allowing us to interpret all the data without any knowledge about the molecular weight distribution. This is no longer possible if one wants to evaluate the complete structure factor; one has to know the exact molecular weight distributions of the D and H polyesters at $t=0$, which requires the use of many parameters. Recently Wu and Gilmer[17] published a paper on the intensity at zero angle. In this section we will make an estimation of the whole scattering curve as a function of time.

Scattering curve at $t=0$

Zimm has evaluated the scattering function $i(q)$ for a polydisperse system in dilute solution satisfying what is called the Zimm–Schulz distribution[18]. For the most probable distribution, i.e. the distribution characterizing the result of a random scission of an infinite chain for which n_n, n_w and n_z are like 1:2:3, $i^{-1}(q)$ plotted as function of q^2 is a straight line. Since the de Gennes result shows that in the bulk the inverse scattering curve is the sum of the curves referring to two polyesters at infinite dilution, $i^{-1}(q)$ will also be a straight line if $n_w/n_n=2$, which is the known distribution for statistical polycondensation[19]. This means that in this case equations (9) and (10) represent the complete scattering curve and not only its asymptotic part. Therefore the inequality $qR>1$ is useless.

Scattering curve at large t

In a recent paper[13] the intensity scattered by a multiblock Gaussian copolymer was calculated and a formula given for the scattered intensity when the blocks are polydisperse and their number sufficiently large. This formula can be used for our problem since the initial mixture of homopolyesters is rapidly transformed into a multiblock copolyester. Following the notation of Reference 13 we write

$$i(q)=x(1-x)\frac{2}{\lambda}\left[1-\frac{1}{\lambda nx(1-x)}\right.$$

$$\left.\times\frac{[1-(1+\varepsilon\lambda nx)^{-\varepsilon^{-1}}]\{1-[1+\eta\lambda n(1-x)]^{-\eta^{-1}}\}}{1-(1+\varepsilon\lambda nx)^{-\varepsilon^{-1}}[1+\eta\lambda n(1-x)]^{-\eta^{-1}}}\right] \quad (32)$$

with

$$n=n_D+n_H$$

$$\varepsilon=\frac{n_{wD}}{n_{nD}}-1$$

$$\eta=\frac{n_{wH}}{n_{nH}}-1$$

and

$$\lambda=\frac{q^2b^2}{6}$$

Since we assume the most probable distribution, $\varepsilon=\eta=1$, equation (32) becomes

$$\frac{1}{i(q)}=\frac{q^2b^2}{12x}+\frac{1}{2}\left[\frac{1}{nx^2(1-x)^2}\right] \quad (33)$$

We also obtain a straight line for $i^{-1}(q)$ as a function of q^2. This is valid if the number of blocks per chain is large enough, but has been evaluated assuming that each block can be considered as a Gaussian chain. If this result is compared with equation (15) in which the value of z_0 has been replaced by z obtained from equation (18) (neglecting z_0, which is supposed to be small), one sees that they are strictly identical since by definition the n of equation (32) is equal to S/N_T. This shows that both approaches lead to the same result.

This discussion shows that for the most probable molecular weight distribution one obtains a straight line in the $i^{-1}(q)$ *versus* q^2 plot for all qs in the two limiting cases: either at $t=0$ according to equation (7) or if the number of units per segment is small compared with the total degree of polymerization n_T, in which case equation (32) yields a straight line again with, of course, a different intersection. It is probable that between these two limits, i.e. at the beginning of the transesterification reaction, this is not the case. For instance, if the first mechanism is valid at the beginning, two chains of number average degree of polycondensation n will be transformed into two chains with average degree of polycondensation $(n/2+n/2)$; in the second case the degree of polycondensation will be $n+n/2$ for one of the chains and $n/2$ for the second. These differences can be calculated but this is useful only if the experiments are precise enough to show a significant difference between a straight line and the experimental data.

GENERALIZATION TO DIFFERENT COPOLYESTERS

If instead of using a mixture of polyesters differing only by their contrast factor one uses two different polyesters, changes have to be introduced into our results. The major difficulty is due to the incompatibility of copolyesters of different chemical compositions. If the interaction coefficient χ is large, the polyesters will not yield a homogeneous mixture and the transesterification reaction will take place at the interfaces. As this proceeds, the incompatibility diminishes and the copolyesters become miscible in all proportions. This is an interesting process but outside the scope of this work. Even if we assume that the polyesters are compatible two difficulties remain. First, one has to use the number of monomers n_a, n_b to characterize the copolyesters since they are essential in order to write kinetic equations. If these monomers have different volumes and different statistical elements, the equations have to be modified to take these differences into account. This is not a real problem but the introduction of these additional constants make the equations a little more complex. Second, in equations (20) and (20′) it has been assumed that $k_+=k_-$. This is no longer exact and becomes evident if one writes the kinetic equation

$$\text{A–A}+\text{B–B}\rightleftharpoons 2\text{A–B}$$

The calculation with two different rates has been done by Olbrich[20]. One loses the single exponential term, which is replaced by a combination of two exponentials but, qualitatively, the results are similar.

CONCLUSION

In this paper we have presented a theoretical analysis of the changes in neutron intensity scattered by a mixture of two polyesters subjected to a transesterification reaction. Assuming that the chains are Gaussian, which is justified for macromolecules in bulk, we have shown that it is possible to obtain the kinetical constant of the reaction. The neutron scattering technique is probably the most suitable for collecting such information. A few laboratories are already working on this experimental problem. We hope that these theoretical considerations will be useful for a better understanding of the reaction mechanisms.

ACKNOWLEDGEMENTS

We would like to thank Dr P. Rempp for fruitful discussions. One of the authors (H.B.) thanks the Alexander von Humboldt Stiftung who gave him the opportunity of participating in this work during his stays in Mainz, Hamburg and Freiburg.

REFERENCES

1 Wu, W., Wiswe, D., Hahn, K. and Zachmann, H. G. *Bull. Am. Chem. Soc.* 1984, **29**, 241

2 Wu, W., Wiswe, D., Hahn, K. and Zachmann, H. G. *Polymer* 1986, **26**, 655

3 McAlea, K. P., Schultz, J. M., Gardner, K. H. and Wignall, G. D. *Polymer* 1986, **27**, 1582

4 Gilmer, J. W., Wiswe, D., Zachmann, H. G., Kugler, J. and Fischer, E. W. *Polymer* 1986, **27**, 1391

5 Kugler, J., Gilmer, J. W., Wiswe, D., Zachmann, H. G., Hahn, K. and Fischer, E. W. *Macromolecules* 1987, **20**, 1116

6 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, 1979

7 Benoit, H. in 'Scattering, Deformation and Fracture in Polymers' (Eds. G. D. Wignall, B. Crist, T. P. Russell and E. L. Thomas), *Mater. Res. Soc. Proc.* 1987, **79**

8 Debye, P. Technical Report CR 637, Office of Rubber Reserve, 1945

9 Benoît, H. *J. Polym. Sci.* 1953, **11**, 507

10 Leibler, L. *Macromolecules* 1980, **13**, 1602

11 Leibler, L. and Benoît, H. *Polymer* 1981, **22**, 195

12 Benoît, H., Wu, W., Benmouna, M., Mozer, B., Bauer, B. and Lapp, A. *Macromolecules* 1985, **18**, 986

13 Benoît, H. and Hadziioannou, G. *Macromolecules* 1988, **21**, 1449

14 Casassa, E. E. *J. Polym. Sci. A* 1965, **3**, 605

15 Rempp, P. and Strazielle, C. 'Encyclopedia of Polymer Science and Engineering', Vol. 9, John Wiley, New York, 1987

16 Hadziioannou, G. and Benoît, H. unpublished results

17 Wu, W. and Gilmer, J. W. *Polym. Commun.* 1987, **28**, 202

18 Zimm, B. H. *J. Chem. Phys.* 1948, **16**, 157

19 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, 1971

20 Olbrich, E. private communication

21 Kugler, J. *Thesis*, Mainz, 1988