Study of the Transesterification of a Main-Chain Mesomorphic Polyester by Small-Angle Neutron Scattering

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ABSTRACT: The phenomenon of transesterification of a mesomorphic polyester is investigated in the isotropic and the nematic phase using small-angle neutron scattering (SANS). In the isotropic phase, the kinetic experiment results are in good agreement with the theoretical predictions of Benoît et al. for the determination of rate constant and activation energy of the transesterification process. In the nematic phase, SANS in the intermediate scattering vector range is not sensitive to the transesterification. This is perhaps due to the cylindrical shape adopted by the polymer chain. The results are discussed as a function of the molecular weight for two different spacers.

1. Introduction

Small-angle neutron scattering (SANS) is an efficient tool for determining the molecular conformation of polymers in the condensed state using a mixture of deuterium-labeled (D) and nonlabeled (H) polymers. In the past 20 years, SANS has been successfully used to measure the chain dimension in the glassy and semicrystalline states[1-4] and in the liquid crystalline state.[5,6] However, chain conformation studies of the main-chain mesomorphic polymer in the liquid crystalline state are rare.[6,7] Nevertheless, theoreticians[8-12] have proposed a "hairpin" conformation model for this type of polymer in the nematic phase by using the wormlike chain assumption. The so-called hairpin is a chain arrangement resulting from an interplay of nematic alignment and the tendency of the polymer to maximize entropy. On the one hand, the chain tends to align entirely along the nematic direction to minimize energy. On the other hand, if the wormlike chain is sufficiently flexible, de Gennes[8] has suggested that it will undergo rapid reversals in direction to form hairpins. Such a structure has never been observed, but preliminary investigations by SANS[6,7] have indicated the possibility of the existence of this structure in a mesomorphic aliphatic–aromatic polyester. Following this initial work, we have undertaken a new study of the conformation of this type of polyester in the nematic phase. The advantages of this main-chain mesomorphic polymer are its relatively low transition temperatures and its high solubility in common solvents. The latter allows us to obtain a homogenous mixture of H and D polymers and to determine the molecular weights with standard procedures. The polyesters used are a series of poly(2,2′-dimethyl-4,4′-dioxyazoxybenzene–alkanedioyls).

The samples for SANS experiments are mixtures of H and D polymers in which microvoids have to be eliminated to avoid strong spurious central scattering. To obtain a homogeneous sample, the initial method involves heating the mixture at high temperature (in the isotropic phase) under vacuum for about 10 h. The first SANS experiments on these treated samples gave unexpected values of the weight-average molecular weights, M_w, which were much smaller than those determined by SEC–LS (size exclusion chromatography–on-line light scattering). A comparison of the values of the molecular weights of the polyesters before and after the sample preparation (thermal treatment) is shown in Table I. According to the SEC–LS measurement, the value of M_w is doubled after the sample preparation while the variation of the number-average molecular weight, M_n, is not significant. Moreover, the M_w value determined by SANS is found to be much smaller than that measured by SEC–LS. These results demonstrate that an important interchange reaction between chains occurred during the sample preparation. Similar observations have been made recently by other authors with different polyesters.[13,14] This interchange reaction between polyesters is called *transesterification*. It is the random scission and recombination of the carboxyl groups ((C=O)O) in the polyesters induced by heating, but the recombination does not necessarily take place between the same subchains which together constituted the initial molecule. As a result, partially deuterated polyesters were produced in our case from the mixture of D and H polyesters. SEC–LS measurements cannot distinguish the D from the H subchains; however, SANS can make such a distinction and after transesterification gives M_w(SANS) $<M_w$(SEC–LS). Thus transesterification does not change the number-average molecular weight of the mixture but broadens the molecular weight distribution.

The existence of partially deuterated polymers in the sample makes the interpretation of SANS data very difficult and is an obstacle to the investigation of the chain conformation. Therefore, the process of transesterification has to be studied in order to understand and control the extent of the reaction and to develop a sample preparation procedure for SANS experiments. Surprisingly, although transesterification in polyesters had been discussed 50 years ago,[15] the kinetics of this reaction was investigated successfully only recently by SANS.[13,14,16] Benoît et al.[16] have established a theory to interpret the SANS data which gave the kinetic parameters of transesterification for PET (poly(ethylene terephthalate))[13] and an aromatic tercopolyester.[14] This paper reports the results of investigations of the transesterification of the main-chain mesomorphic polyesters discussed above, which present lower transition temperatures than those of other polyesters.[13,14] In the following (section 2) the theory of transesterification will be briefly recalled from the SANS point of view. In the experimental section (section 3) the sample preparation and the neutron setup will be described. The results

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Table I
Molecular Weights of the 50:50 Mixture of Hydrogenated and Deuterated Poly(2,2′-dimethyl-4,4′-dioxyazoxybenzene-dodecanedioyl) before and after Sample Preparation[a]

	M_n (SEC–LS)	M_w (SEC–LS)	M_w (SANS)
original powder	13600	16100	
sample after preparation	12600	28100	6340

[a] M_n = number-average molecular weight; M_w = weight-average molecular weight.

concerning the transesterification observed in the isotropic phase and in the nematic phase will be discussed in section 4.

2. Theory

Benoît et al.[16] consider the effect of transesterification in a mixture of x (number fraction) D and $(1 - x)$ H polyesters. The chains are assumed to be Gaussian with a statistical step length b and a radius of gyration R_G. From random phase approximation[17,18] they predict for the SANS intensity, $I(q)$ (in units of cm^2/cm^3), in the intermediate range of q (scattering vector) the following relation:

$$\frac{K_I}{I(q)} = \frac{q^2b^2}{12} + \frac{1}{2}\left(\frac{1}{n_D(t)} + \frac{1}{n_H(t)} - \frac{1}{n_T{}^\circ}\right) - 2\chi \qquad (1)$$

$$R_G{}^{-1} < q < b^{-1}$$

$$K_I = x(1 - x)(a_H - a_D)^2 N_T$$

where $n_D(t)$ and $n_H(t)$ are the number-average degrees of polymerization of the D and H polyesters (either whole chains or blocks), respectively, at time t after the beginning of the transesterification. N_T is the total number of monomers per unit volume. $(a_H - a_D)^2$ is the contrast factor, where a_H and a_D are the coherent scattering lengths of the hydrogenated and deuterated monomers, respectively. χ is the Flory–Huggins interaction parameter between the H and D monomers, which is generally considered to be zero as long as the molecular weight of polymer is not too high. $n_T{}^\circ$ is the initial number-average degree of polymerization of the total sample:

$$\frac{1}{n_T{}^\circ} = \frac{x}{n_D{}^\circ} + \frac{1 - x}{n_H{}^\circ}$$

Thus the model predicts a linear variation of $I^{-1}(q)$ as a function of q^2, the slope of which is time independent while the intercept $I^{-1}(0)$ is an increasing function of time.

In the reaction kinetics, the rate constant k is an important parameter. It can be related to another parameter τ, the relaxation time for the approach to the equilibrium distribution of H and D monomers following the relation

$$\tau = 2/(kN_T) \qquad (2)$$

From eq 1, the extrapolation of the curve in Zimm representation ($I^{-1}(q)$ versus q^2) to zero q value gives the intercept $Z(t)$ predicted to be

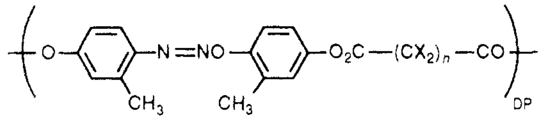
$$\frac{1}{I(0,t)} = Z(t) = Z(0) + \frac{1}{2K_I}\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\} \qquad (3)$$

$$Z(0) = \frac{1}{2K_I}\left(\frac{1}{n_D{}^\circ} + \frac{1}{n_H{}^\circ} - \frac{1}{n_T{}^\circ}\right) \qquad (4)$$

Consequently, from the t variation of $Z(t)$ the relaxation time τ and the initial number-average degree of polymerization of the polymer can be measured. The statistical step length b can be obtained from the slope of the curve $I^{-1}(q)$ versus q^2 if the number of statistical units in a chain is known.

3. Experimental Section

Synthesis of Polymers. The main-chain mesomorphic polyesters have the following structure:



where X is either H or D; DP represents the number-average degree of polymerization. The aliphatic part $(CX_2)_n$ is called the "spacer" in the mesomorphic polymer. When $n = 8$, the polyester is named PE8-H for the hydrogenated sample and PE8-D for the deuterated sample in the following text. Similarly, the polyester is named PE10-H or PE10-D when $n = 10$. The polyester samples were prepared from a diphenol and a hydrogenated or deuterated aliphatic diacid dichloride.[19] The diphenol 4,4′-dihydroxy-2,2′-dimethylazoxybenzene was synthesized from 3-methylphenol.[20] The diacid dichlorides were prepared from the corresponding acids and oxalyl chloride. The hydrogenated diacids were obtained from commercial sources. The deuterated diacids were obtained by catalytic H/D exchanges on aliphatic diacids using Pt/C in NaOH/D_2O at 180–200 °C under high pressure for about 10 days.[21] This procedure leads to 91–94% deuteration of the diacids. The degree of the deuteration was measured by ^1H-NMR (nuclear magnetic resonance) at ICSN (Gif-sur-Yvette) and taken into account in the determination of the contrast factor in K_I (eq 1). The polyesters were synthesized by interfacial polycondensation from diphenol and diacid dichlorides. Each polyester thus obtained was purified by dissolving in chloroform, filtering, and precipitating drop-by-drop into ethanol 10 times the volume of the chloroform. The polyesters, after being dried under vacuum, were fractionated by using dichloroethane–methanol as the solvent–precipitant. The molecular weight distributions of the polyester fractions were measured by SEC-LS on line at ICS–CRM (Strasbourg) from polyester solutions in tetrahydrofuran. The M_n values obtained by this technique are overestimated and the M_w/M_n underestimated. The M_w/M_n used are the averages of those measured by SEC–LS and those obtained by calibration of standard samples of polystyrene. The M_n are then corrected to a first approximation (about 5%) by the averaged M_w/M_n and the M_w measured. All the values of M_n and M_w/M_n in this paper are thus corrected. DSC (differential scanning calorimetry) is used to determine the phase transition temperatures. The results are summarized in Table II. Notice the narrow molecular weight distribution obtained for each fraction.

Sample Preparation and Small-Angle Neutron Scattering. Each mixture of H and D polyesters was prepared by dissolving polyesters with a similar degree of polymerization at 50:50 weight ratio in chloroform. The solvent was then evaporated, and the solid obtained was dried under vacuum. The homogenous sample was prepared with the following improved method in order to shorten the thermal treatment and to neglect the transesterification during the sample preparation. The polyester mixture was molded at the temperature just below T_{CN} into a disk (1 mm thick and 15 mm diameter) and then pressed at 10 000 psi at T_{CN} for 15 min. The disk specimen was placed in a quartz cell installed in a special oven for the neutron experiment. The small-angle neutron scattering data were obtained on the PAXY spectrometer in the Orphée reactor (Laboratoire Léon Brillouin, Saclay). The incident wavelength used was 5 Å, and the distance between the detector and the sample was 3 m. The range of q values was 0.016–0.16 $Å^{-1}$. For studies in the isotropic phase, the specimen was heated within 10 min to the selected temperature, and the scattering data were collected while annealing at this temperature. For studies in the nematic phase, the specimen was heated to the lowest temperature of the isotropic phase for several minutes and then cooled down to the given temperature in the nematic phase before data acquisition.

Table II
Characterization Results of the Polyester Samples by SEC–LS and DSC

	SEC–LS			DSC			
				heating rate 2 °C/min		cooling rate −2 °C/min	
	M_n	M_w	M_w/M_n	T_{CN}[a] (K)	T_{NI}[a] (K)	T_{IN}[a] (K)	T_{NC}[a] (K)
PE8-D DP21	9500	11500	1.21			461 → 451	402 → 393
PE8-H DP21	9020	11100	1.23			462 → 454	403 → 395
PE10-D DP29	13600	16100	1.18	386 → 398	429 → 438	431 → 425	381 → 372
PE10-H DP28	12800	14900	1.16	385 → 398	429 → 440	432 → 425	381 → 372
PE10-D DP14	6760	7910	1.17	379 → 394	421 → 430	426 → 417	377 → 366
PE10-H DP15	6630	7630	1.15				

[a] T_{CN} represents the transition range from crystalline phase to nematic phase; T_{NC} is its contrary. T_{NI} represents the transition range from nematic phase to isotropic phase; T_{IN} is its contrary.

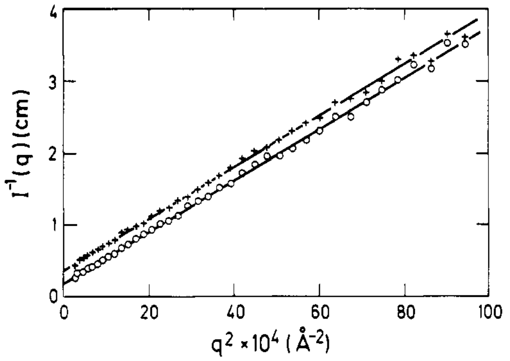


Figure 1. Zimm representation of the scattering intensity ($I^{-1}(q)$ versus q^2) for polyester PE10 DP29 annealed in the isotropic phase at 433 K for 1 h (○) and for 22 h (+). The data are fitted with straight lines.

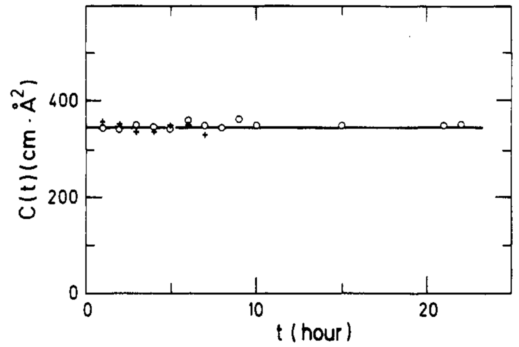


Figure 2. Slopes of the curves in Zimm representation, $C(t)$, versus the annealing time, t, for polyester PE10 DP29 in the isotropic phase at 433 K (○) and at 457 K (+).

The data treatment was carried out using the classical procedure. The background was determined from the weighted sum of the incoherent intensity delivered by a sample made of H polymers and that delivered by D polymers. Absolute calibration was obtained from the direct determination of the number of neutrons in the incident beam.[22] This allowed us to obtain $I(q)$ in cm^{-1}.

4. Results and Discussion

4.1. Transesterification in the Isotropic Phase. The transesterification reaction has been studied during the annealing of the PE8 and PE10 samples in their isotropic phases from the variation of the SANS intensity as a function of time. For each sample, the measurements were taken every 10 min for the first six spectra and every 1 h for the following ones (about 30 acquisitions in total). The parameters of this study are as follows: spacer length of the polyester, $n = 8$ or $n = 10$; molecular weight for sample PE10, DP29 or DP14; temperature for sample PE10 DP29, $T = 433$ K or $T = 457$ K. The molecular weights and the polydispersities of the polyesters are given in Table II together with the values of the corresponding phase transition temperatures. In the isotropic phase, the value of the radius of gyration R_G is 68 Å for PE10 DP29 and 46 Å for PE10 DP14. These values were determined, a fortiori, by SANS in the Guinier range when the study of the transesterification was achieved. For these measurements the transesterification effects were negligible as verified by the values of M_w determined during the same time by SANS (M_w(SANS) = 17 200 while M_w(SEC–LS) = 16 100 for the D polyester PE10 DP29).

Let us first discuss the typical results obtained for the sample PE10 DP29 at 433 K. The R_G value of 68 Å shows that the SANS study was carried out in the intermediate q range ($qR_G > 1$). Figure 1 shows the Zimm representation ($I^{-1}(q)$ against q^2) for two annealing times, 1 and 22 h. The data are very well fitted with a straight line:

$$I^{-1}(q) = q^2C(t) + Z(t)$$

in the q^2 range of 5×10^{-4} to 1×10^{-2} Å^{-2}. The curves obtained at different annealing times are parallel. This is confirmed from the variation of the slopes, $C(t)$, with time (Figure 2)

$$C(t) = (0.1 \pm 0.2)t + (356 \pm 2) \quad (\text{cm Å}^2)$$
$$(t \text{ in hours}, T = 433 \text{ K})$$

which is about zero and temperature independent. This result is in very good agreement with theory,[16] in which the slope is predicted to depend only on the length of the statistical unit, but rather different from that observed by MacDonald et al.[14] with a tercopolyester. According to eq 1, the statistical length can be obtained from the slope. This procedure uses the monomer number instead of the number of statistical units. The value thus obtained ($b = 26$ Å) corresponds to an efficient statistical length. The b values are nearly the same at $T = 433$ K and $T = 457$ K (see Figure 2).

The variation of the intercept $Z(t)$ is shown in Figure 3 for both temperatures, $T = 433$ K and $T = 457$ K: $Z(t)$ are linear functions of t. This result is due to the slow rate of the transesterification reaction and provides an experimental reason to use in eq 3 the first term of the development of the exponential function. Equation 3 thus becomes

$$Z(t) = Z(0) + \frac{t}{2K_I\tau} \qquad t \ll \tau \tag{5}$$

Following this equation, the experimental data $Z(t)$ can be fitted as (see Figure 3)

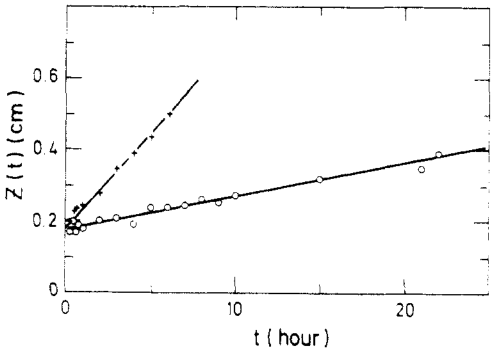


Figure 3. Extrapolations to $q = 0$ of the curves in Zimm representation, $Z(t)$, versus the annealing time, t, for polyester PE10 DP29 in the isotropic phase at 433 K (○) and at 457 K (+). The straight lines correspond to the fits with linear functions.

$$Z(t) = (0.18 \pm 0.02) + (0.0089 \pm 0.0002)t \quad \text{(cm)} \quad (t \text{ in hours, } T = 433 \text{ K})$$

$$Z(t) = (0.18 \pm 0.02) + (0.088 \pm 0.002)t \quad \text{(cm)} \quad (t \text{ in hours, } T = 457 \text{ K})$$

The relaxation times, τ, given in Table III are deduced from N_T and K_I values ($K_I = 0.149$ for PE10). N_T is obtained from the sample density ($\rho = 1.28 \pm 0.05$ g/cm^3) estimated from the filling of a cell. The τ values are very sensitive to temperature since $\tau = 38$ h at 457 K and 10 times greater at 433 K. For our polyester, the transesterification reaction is very slow compared to the reaction observed with PET[13] at higher temperatures (about 550 K), for which the τ values are of the order of 10 s.

To specify the process of transesterification, the number-average degree of polymerization of deuterated chains or blocks at time t after the beginning of the reaction, $n_D(t)$, is compared to that of the initial chains, $n_D{}^\circ$. The number of efficient scissions per chain $S'(t)$ which cut up the H and D chains and produce the H and D block copolymer is[16]

$$S'(t) = 2x(1-x)n_D{}^\circ \frac{t}{\tau} \qquad t \ll \tau \tag{6}$$

Then the variation of the value of $n_D(t)$ as a function of time is

$$\frac{\Delta n_D(t)}{n_D{}^\circ} = \frac{-S'(t)}{1 + S'(t)}$$

For example, 1 h after the beginning of the transesterification $S'(t)$ is about 0.04 times/chain and $\Delta n_D(t)/n_D{}^\circ$ is about −4% for polyester PE10 DP29 at 433 K in the isotropic phase. On the average, one efficient scission for each chain requires 25 h of annealing, and consequently the number-average molecular weight is 50% of its initial value.

Concerning our initial question: what is the maximum annealing time afforded to prepare and to study a sample with negligible effects of transesterification?, the answer is about 1 h at 433 K but is very temperature dependent.

Table III
Relaxation Times (τ) and Rate Constants (k) of Transesterifications for PE10 DP29

T (K)	τ (h)	$k \times 10^{20}$ (s^{-1} cm^3)[a]
433	377 ± 10	1.15 ± 0.05
457	38 ± 1	11.4 ± 0.5

[a] The units of the rate constants are per second per monomer concentration (1/cm^3).

Table IV
Relaxation Times (τ) and Rate Constants (k) of Transesterifications for Two Different Molecular Weight Samples of PE10 at 433 K

M_n(PE10-D)	τ (h)	$k \times 10^{20}$ (s^{-1} cm^3)
6760	393 ± 10	1.10 ± 0.05
13600	377 ± 10	1.15 ± 0.05

Table V
Relaxation Times (τ) and Rate Constants (k) of Transesterifications for Two Polyesters with Different Spacer Lengths (n = 8 and n = 10) at 457 K

spacer length	τ (h)	$k \times 10^{20}$ (s^{-1} cm^3)
n = 8 (PE8 DP21)	39 ± 1	10.4 ± 0.5
n = 10 (PE10 DP29)	38 ± 1	11.4 ± 0.5

The rate constants k, obtained from eq 2, are given in Table III for 433 and 457 K. According to the Arrhenius equation

$$k = A \exp(-E/RT)$$

the activation energy E can be calculated

$$E = 157 \pm 4 \text{ kJ/mol}$$

Thus the dependence of rate constant k on the temperature T of polyester PE10 DP29 is

$$k = 0.102 \exp\left(\frac{-18.9 \times 10^3}{T}\right) \quad (\text{s}^{-1}\ \text{cm}^3)$$

The value of E is in good agreement with those found for PET[13] (E = 152 kJ/mol) and for a tercopolyester[14] (E = 157 kJ/mol).

In the paper of Kugler et al.[13], the rate constant k' was defined differently:

$$u = k't \tag{7}$$

u is the number of times each chain has undergone transesterification at time t, i.e., the number of all scissions (efficient and nonefficient) per chain. The relation between u and $S'(t)$, the number of efficient scissions per chain, is

$$2x(1-x)u = S'(t) \tag{8}$$

Equations 8 and 6 give

$$u = (n_D{}^\circ/\tau)t$$

Then

$$k' = \frac{n_D{}^\circ}{\tau} = \frac{n_D{}^\circ N_T}{2}k \tag{9}$$

For example, $k' = 2.2 \times 10^{-5}$ s^{-1} at T = 433 K and $k' = 2.2 \times 10^{-4}$ s^{-1} at T = 457 K for PE10 DP29. The transesterification reactions under our experimental conditions are much slower than that of PET in ref 13 ($k' \geq 0.067$ s^{-1}).

Table IV gives the kinetic parameters of the transesterification for two different molecular weight samples of polyester PE10 at 433 K. A doubling of the molecular weight does not change significantly the relaxation time and rate constant. The kinetics of the transesterification seems to be independent of the molecular weight of the initial polyester. This result is contrary to that obtained by McDonald et al.[14]. Further experiments are being undertaken to confirm this result.

The effect of the spacer length on the transesterification was examined by comparing the kinetic parameters of the polyesters PE8 and PE10 (Table V). The values of the kinetic parameters of the transesterification are not sensitive to a change in spacer length from (CH$_2$)$_8$ to

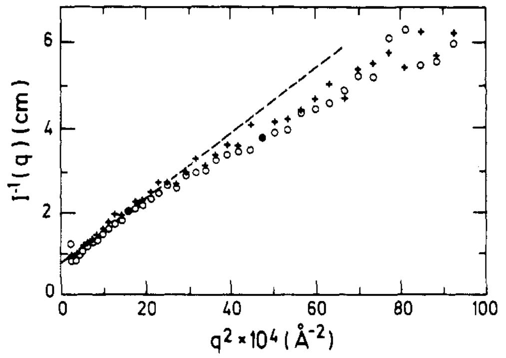


Figure 4. Zimm representation of the scattering intensity $I^{-1}(q)$ versus q^2 for polyester PE8 DP21 annealed in the nematic phase at 433 K for 2 h (○) and for 16 h (+). A straight line is not appropriate to fit the data in this phase.

$(CH_2)_{10}$. The small differences observed might be due to the different viscosities of the samples in bulk.

Finally, note that the q^2 dependence of $I^{-1}(q)$ for all the q range (see Figure 1) is quite a surprising result. Indeed, even if our polyester chains are assumed to have a Gaussian conformation, they are too monodisperse at the beginning of the transesterification and too short to give only one slope in the Zimm representation. As a matter of fact, for a Gaussian coil, the curve $I^{-1}(q) = f(q^2)$ has to have one slope in the Guinier range (intercept $1/M_w$) and another slope in the intermediate range (intercept $1/(2M_n)$). If $M_w = 2M_n$ the two slopes overlap; but this is not the case here ($M_w = 1.18M_n$). This remark is confirmed from the value of M_n obtained for polyester PE10 DP29 from $Z(0)$: M_n(SANS) = 8800, while M_n(SEC–LS) = 13 600. Since our polyesters are semiflexible chains, the straight line observed may be a coincidence corresponding to a crossover between a q^2 law for small q values and the scattering of a cylinder at large q values (see next section). In any case, the values of the relaxation time and the rate constant would remain similar.

4.2. Transesterification in the Nematic Phase. Polyesters PE8 and PE10 have been studied in the nematic phase at T = 433 K and T = 408 K, respectively. An example of the scattering data in Zimm representation is given in Figure 4. This figure shows that a fit of the data with a linear function of q^2 is clearly inadequate. In addition, the signals do not vary significantly with time.

It is reasonable to assume a stretched conformation of the chain in the nematic phase; a cylinder model is used to try to fit the data. The following form for the intensity[23] is used:

$$I(q) = \pi\frac{K_I}{m}\left(\frac{M}{L}\right)\frac{1}{q}\exp\left(-\frac{1}{4}q^2R^2\right) \qquad L^{-1} \ll q \leqslant R^{-1} \qquad (10)$$

where L is the height, R the radius, and M the total molecular weight of the cylinder. m is the molecular weight of monomer.

Figure 5 shows the experimental data of polyester PE8 DP21 annealed for 2 h at 433 K fitted with eq 10 using a nonlinear regression method. The fit is clearly good and gives the value of the cylinder radius R = 11 ± 1 Å and the molecular weight per cylinder height M/L = 27 ± 1 (Da Å^{-1}). The data at different times are fitted in the same way with eq 10 and, within experimental error, give the same value of R and M/L. The fits of the data of polyester PE10 DP29 annealed in the nematic phase at 408 K give the same results with cylinder radius R = 11 ± 1 Å and molecular weight per cylinder height M/L = 32 ± 1 (Da Å^{-1}). At the same temperature T = 433 K PE8 is in the nematic phase, but PE10 is in the isotropic phase and the presence of the transesterification of PE10 is evident (Figures 1–3). Assuming that the transesterification takes place also in polyester PE8 at 433 K in the nematic phase, to a certain extent of the reaction, the data can always be interpreted with the thin cylinder model (eq 10) in the intermediate q range. Thus the chains possess a cylinder conformation, and so do the blocks of the chain. The transesterification modifies only the lengths of the D and H blocks in the chain, i.e., the height of the cylinder but not the linear density of the blocks. So $I(q)$ would not vary with the annealing time in any case according to eq 10.

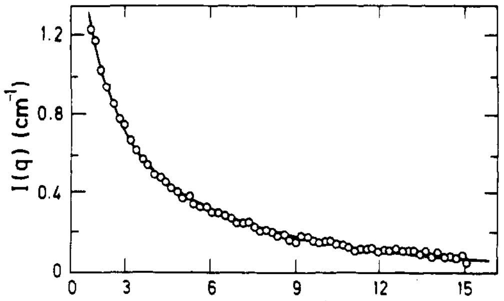


Figure 5. Scattering intensity $I(q)$ versus q for polyester PE8 DP21 annealed in the nematic phase at 433 K for 2 h. The line is the best fit with a cylinder model (see eq 10).

We have also tried to fit the experimental data with the following equation:

$$\frac{1}{I(q)} = \frac{m}{K_I}\frac{1}{i(q)}\exp\left(-\frac{1}{4}q^2R^2\right) \qquad L^{-1} \ll q \leqslant R^{-1} \qquad (11)$$

$$\frac{1}{i(q)} = \frac{q}{\pi(M/L)} + \frac{2}{\pi^2 M_n} \qquad (12)$$

Equation 12 has been derived[24] in order to take into account rod ends. The best fit of the data is obtained with a negligible value of the second term of eq 12 and similar values of M/L and R as obtained with eq 10. Thus it is not possible to determine τ from a procedure similar to that used for the isotropic phase.

Our conclusion is in the nematic phase the SANS response is not sensitive to the transesterification reaction in the q range used here. Nevertheless, the extent of the transesterification in the nematic phase can be tested as follows: First, $I(q)$ is measured in the isotropic phase of the sample. Then the sample is annealed in the nematic phase for the time needed and finally $I(q)$ is measured for the sample rapidly heated to the isotropic phase. If the two measurements overlap, the transesterification in the nematic state should not be significant during this annealing time. Such a test was made for a polyester with the spacer $(CH_2)_{11}$ (PE11). Its transition temperatures are $T_{IN} = 402 \rightarrow 397$ K and $T_{NC} = 353 \rightarrow 333$ K by DSC (−2 °C/min). The sample was annealed in the nematic phase at 387 K for about 10 h. The scattering intensities in the isotropic phase before and after the annealing are the same in the limit of confidence of the error bars. So the transesterification of PE11 in the nematic phase is very slow and can be neglected in the time scale of 10 h.

Now we discuss the chain conformation in the nematic phase. For a totally stretched polyester chain (PE8 or PE10) the value of M/L is estimated to be 18 (Da Å^{-1}) and that of R to be about 3 Å. Here the values of M/L and R obtained by fitting the experimental data with the cylinder model are M/L = 27 (Da Å^{-1}) for PE8 and M/L = 32 Da Å^{-1} for PE10 and R = 11 Å for both polyesters. So, we can imagine two possible models for the chain conformation in the cylinder. The first one is the wavy chain in which the spacers of the monomers involve an important population of gauche conformations. The coexistence of the gauche and trans conformations in the spacers has been proposed by Samulski et al.[25] from their studies of this type of polyester by ^{2}H NMR. The second possible model for the chain conformation is the existence of hairpin. We are not able to choose between these models.

5. Conclusion

The transesterification kinetics of a main-chain mesomorphic polyester in the isotropic phase is well evaluated by the SANS method in the intermediate scattering vector range. The kinetic parameters are very sensitive to the temperature, and the activation energy is 157 kJ/mol. The initial molecular weight of the polyester has little influence on the reaction kinetics. For the polyesters with spacer $(CH_2)_8$ and $(CH_2)_{10}$ nearly the same reaction kinetics has been obtained. In the nematic phase, the chain seems to adopt a cylindrical conformation, and, in the q range used here, it is difficult to determine from SANS data the kinetics of the transesterification reaction, if it occurs. However, since the number of scissions increases strongly with increasing temperature, the value of the relaxation time obtained at the lowest temperature of the isotropic phase can be reasonably used as a minimum reference value for studies in the nematic phase. The extent of the transesterification in the nematic phase can be also estimated by the procedure proposed (section 4.2.). For the main-chain polyester discussed here, it is possible to prepare and to study samples where the transesterification reaction is negligible in order to get the chain conformation. Such studies are currently being carried out at the Laboratoire Léon Brillouin.

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