

Small-angle neutron scattering of partially segregated amorphous poly(ethylene terephthalate)

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(Received 6 June 1984)

Deuterated poly(ethylene terephthalate) (DPET) was synthesized from deuterated ethylene glycol and deuterated dimethyl terephthalate which was derived from 1,4-dibromobenzene. Amorphous specimens for small-angle neutron scattering (SANS) were prepared by solution blending the DPET with the hydrogenated PET and subsequently melt pressing. The SANS results suggested the occurrence of both segregation and transesterification between the deuterated and hydrogenated species. An expression for the scattered intensities from partially segregated blends has been derived. Using this expression the average molecular weight, the radius of gyration, and the size of the segregation domains, can be determined quantitatively from the SANS data.

(Keywords: neutron scattering; segregation; cluster; poly(ethylene terephthalate); blends; transesterification)

INTRODUCTION

Small-angle neutron scattering has been used extensively to evaluate the conformation of polymer molecules in their bulk states. Most small angle neutron scattering (SANS) studies reported so far were conducted on polymers of addition type, e.g., polyethylene, polypropylene, polystyrene, etc.; interchain exchange reaction between the deuterium labelled species and the hydrogenated ones can be avoided during the preparation of the bulk specimens. Polymers of condensation product such as nylons and polyesters are of great commercial importance, however, no SANS result has been reported.

There arise two problems when one studies poly(ethylene terephthalate) (PET). First, exchange reactions occur between the deuterated chains and the protonated ones. This has been deduced from different chemical examinations¹ as well as from changes in the molecular weight distribution observed during melting of mixtures of two materials with different molecular weights². Second, partial segregation between the deuterated labelled chains and the unlabelled chains takes place. Such segregation effects have been observed frequently and are well documented in bulk specimens³⁻⁶. Hitherto crystalline polymers are the ones with the most noticeable segregation effects as judged from their SANS results. However, as shown by the SANS results to be reported in

the following, in the case of PET, severe segregation of the labelled chains also took place in amorphous specimens. Therefore, for any further investigation it is essential to have available a theoretical treatment for evaluation of the results obtained from segregated materials.

In cases where the extent of segregation of the labelled chains is limited, the SANS intensities can be adequately described by an equation derived from a random phase approximation (RPA) scheme^{7,8}. According to the RPA result the enhancement of the scattered intensities due to the segregation effect follows a simple rule; the inverse of the intensities decreases uniformly over the entire h range where h is the scattered vector defined as $(4\pi/\lambda)\sin\theta$ with its ordinary meaning. The SANS results of the amorphous PET specimens to be reported apparently deviate from the RPA equation, presumably owing to an extent of segregation that is too severe to be modelled by scattering equations based on mean field derivations. Certain mean field approximations were adopted in the derivation of the equation^{7,8} mentioned above.

Attempts have been made in the past to model the scattering intensities from segregated blends by summing up the intensities caused by the concentration fluctuations and by the structure factor of the average single chain⁹. The contributions to the total intensities from each factor were further weighted by the empirical factors α and $1-\alpha$. No physical insight can be obtained from such an empirical approach.

Consequently, a general expression relating the struc-

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tural parameters of partially segregated blends and the resultant scattered intensities was derived and is presented in the following section. SANS data from the amorphous PET specimens were analysed using this newly derived equation.

THEORETICAL DERIVATION

The systems under consideration are blends of deuterated and hydrogenated chains with equal molecular weight n in terms of the number of the statistical segments. The scattering lengths for each segment are denoted by b_D and b_H for the deuterated and the hydrogenated species respectively. The scattered intensities can be expressed in the Zernike-Prins form

$$I(h) = (b_D - b_H)^2 \left[N_D \overline{f_n^2(h)} - \frac{N_D^2}{V} \overline{f_n(h)}^2 \right] \int (1 - P(r)) \frac{\sin hr}{hr} 4\pi r^2 dr \quad (1)$$

where N_D is the number of D chains within the scattering volume V , $f_n(h)$ is the form factor of each chain, and the function $P(r)$ is the pair correlation function describing the distribution of the centres of mass of either D or H chains.

The difference in the scattered intensities between the segregated and randomly distributed blends originates from the changes of the function $P(r)$ upon segregation. In other words, the scattered intensities of a partially segregated blend will be described in terms of the nonrandom distribution of the centres of mass of the labelled chains. This approach is quite different from others that considered the correlation between statistical segments instead of the centres of mass.

Upon segregation there is an enhancement of the correlation function $P(r)$ over a certain domain characterized by a distance l_c . The concentration of the centres of mass of the D species within the domain is enhanced. However, the concentration outside the domain must be depleted due to the conservation of the total number of D molecules. In the following paragraph, the statements made above will be quantified with the introduction of a two-phase model. The concentrations of the centres of the mass both within and outside the domains are constant and the difference in concentration is given at $\Delta C \bar{N}/V$ in terms of number of centres of mass of D chains per unit volume where \bar{N} is the total number of the molecules in volume V . The fraction of volume occupied by the D chains enriched domains is denoted as ϕ , and consequently, the correlation length a of such a two-phase system follows the simple relation $l_c = a/1 - \phi$ according to the Porod's relation¹⁰. The correlation function dictating the geometric configuration of this two-phase system is simply denoted as $\gamma(r)$. Given the average volume fraction of the D chains within the scattering volume V to be X_D , the corresponding value of the concentration of the centres of mass of D chains per unit volume follows $C_D = X_D$. The local concentration C_h of the D chains within the D chains enriched domains can be expressed as $C_h = C_D + (1 - \phi)\Delta C$; for the depleted domains $C_L = C_D - \phi\Delta C$.

We now proceed to calculate the integration of equation (1) using the structural parameters defined above. There are four different cases encountered during the

calculation of the value of $(N_D^2/V)P(r)$; these cases are characterized by whether the origin and the end of the distance r are located within or outside the domains where the D chains population is enhanced. For each of the four cases, the corresponding value of $(N_D^2/V)P(r)$ is different. Let $[(N_D^2/V)P(r)]_{ii}$ denote the case in which both ends of r are within the domains. From a simple probabilistic consideration¹¹

$$\left[\frac{N_D^2}{V} P(r) \right]_{ii} = \frac{C_h^2 \bar{N}^2}{V} \phi [\phi + (1 - \phi)\gamma(r)] P^0(r) \quad (2)$$

where $P^0(r)$ is the pair correlation function of the centre of mass of an amorphous chain in an ideal blend. Similarly, for the case in which the origin of r is inside that domain and the end of r is outside, one has

$$\left[\frac{N_D^2}{V} P(r) \right]_{i0} = \frac{C_h C_L \bar{N}^2}{V} \phi (1 - \phi) (1 - \gamma(r)) P^0(r) \quad (3)$$

The value of $[(N_D^2/V)P(r)]_{oi}$ has the same expression as shown in equation (3) by using the simple symmetry argument. Finally, for the case that both ends of r are outside the domains one has

$$\left[\frac{N_D^2}{V} P(r) \right]_{00} = \frac{C_L C_L \bar{N}^2}{V} (1 - \phi) (1 - \phi + \phi\gamma(r)) P^0(r) \quad (4)$$

By summing up the expressions for all four cases, one obtains the following equation

$$\left\langle \frac{N_D^2}{V} P(r) \right\rangle = \frac{N_D^2}{V} P^0(r) + \frac{\bar{N}^2}{V} \Delta C^2 \phi (1 - \phi) P^0(r) \gamma(r) \quad (5)$$

where $\langle \rangle$ denotes the average throughout the scattering volume. By placing equation (5) into equation (1), one has a general formula describing the scattered intensities of a partially segregation system as follows

$$\frac{I(h)}{(b_D - b_H)^2} = N_D \overline{f_n^2(h)} - \frac{N_D^2}{V} \overline{f_n(h)}^2 \int (1 - P^0(r)) \frac{\sin hr}{hr} 4\pi r^2 dr + \frac{\bar{N}^2}{V} \Delta C^2 \phi (1 - \phi) \overline{f_n(h)}^2 \int P^0(r) \gamma(r) \frac{\sin hr}{hr} 4\pi r^2 dr \quad (6)$$

The first two terms of equation (6) denote the scattering contribution as if the blend is an ideal mixture, and the third term denotes the additional scattered intensities arising from segregation effects. If one assumes that there are domains completely depleted of D chains⁵, the corresponding value of C_L is zero and ΔC becomes X_D/ϕ . Consequently, the third term of equation (6) reduces to the formula reported elsewhere¹¹. For amorphous blends, the first two terms can be further simplified using the idea of incompressibility¹². The resultant equation has the form:

$$\frac{I(h)}{(b_D - b_H)^2} = \bar{N} X_D X_H \overline{f_n^2(h)} + \frac{\bar{N}^2}{V} \Delta C^2 \phi (1 - \phi) \overline{f_n(h)}^2 \int P^0(r) \gamma(r) \frac{\sin hr}{hr} 4\pi r^2 dr \quad (7)$$

where X_D and X_H are the volume fraction of the de-

uterated and hydrogenated species respectively. The above equation is only applicable to amorphous blends, certain important modifications will be needed for crystalline polymer blends.

It is noteworthy that the two-phase model proposed in the present derivation does not dictate a sharp boundary between these phases with different composition. The current model only requires domains enriched or depleted in terms of the centres of mass of either type of molecule. Even if the domains can be defined with sharp boundaries in view of the centres of mass of the chains, these domain boundaries will still have a smooth transition in terms of the segment density of D and H species. Following the same arguments, if the value of the correlation length, a , of the function $\gamma(r)$ is less than the radius of gyration, R_g , of the average molecules, no depleted domain can be created even by allowing either C_h or C_L equal to zero. This is believed to be the main advantage of treating scattering problems of partially segregated blends in terms of the Zernicke-Prins approach.

To facilitate comparison between the SANS results and equation (7) the following simplifications were introduced:

$$\overline{f_n^2(h)} \simeq \overline{f_n(h)}^2 \simeq n^2 \left(1 - \frac{h^2 R_g^2}{3}\right) \quad (8)$$

The above expression is a typical Guinier approximation. Furthermore, the pair correlation function $P^0(r)$ of amorphous polymers is rather close to unity. Consequently, one can also introduce the following simplification

$$P^0(r)\gamma(r) \simeq \gamma(r) = \exp\left(-\frac{r}{a}\right) \quad (9)$$

The expression for $\gamma(r)$ shown above is a classical one after Debye *et al.* for randomly shaped two-phase mixtures¹³ and the quantity, a , is the correlation length as discussed in the previous part of this work. After combining equations (8) and (9) into equation (7), one has the following relation for the scattered intensities

$$\frac{I(h)}{X_H X_D (b_D - b_H)^2} \simeq \bar{N} n^2 \left(1 - \frac{R_g^2 h^2}{3}\right) \left(1 + \frac{\bar{N} \Delta C^2 \phi(1-\phi) K a^3}{V X_H X_D (1+h^2 a^2)^2}\right) \quad (10)$$

where K is an integration constant that equals 8π . The quantity $\bar{N}n$ is the total number of monomers within the scattering volume V , and is therefore a constant. For further simplification, the quantity χ is defined as

$$\chi = \frac{\bar{N} \Delta C^2 \phi(1-\phi)}{V X_H X_D} K a^3 \quad (11)$$

The quantity $\Delta C^2 \phi(1-\phi)$ can be expressed in terms of the molecular weight n and the Flory-Huggins interaction parameter χ_{HD} between the deuterated and the hydrogenated species if the segregation process follows a classical path described by mean field theory. One has $\Delta C^2 \phi(1-\phi) = X_H X_D - C' C''$ where C' and C'' are the equilibrium composition of the blend. They are the roots of the equation

$$\frac{1}{n} \ln \frac{C}{1-C} + \chi_{HD}(1-2C) = 0 \quad (12)$$

In the present case, the segregation process is compounded with the transesterification reaction resulting in a random block copolymer; equation (12) is not expected to hold true for this case. Therefore, the multiple $n\chi$ will be determined by extrapolating the intensities to zero scattering angle and the remaining parameters, namely a and R_g , will be determined with a straightforward curve fitting process using the following relation and the SANS results in Zimm plots

$$\left[\frac{I(h)}{\bar{N} n X_H X_D (b_D - b_H)^2} \right]^{-1} = \frac{1}{n} \left(1 + \frac{h^2 R_g^2}{3}\right) \left(1 + \frac{\chi}{(1+h^2 a^2)^2}\right)^{-1} \quad (13)$$

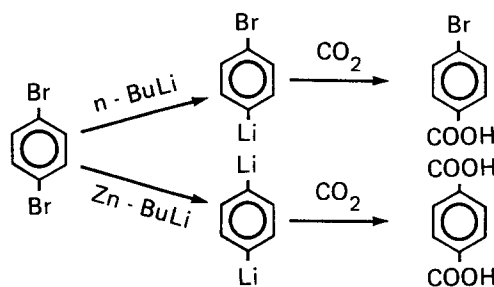
EXPERIMENTAL PROCEDURES AND RESULTS

Synthesis of deuterated poly(ethylene terephthalate)

The deuterated poly(ethylene terephthalate) was synthesized by transesterification of deuterated dimethyl terephthalate and deuterated ethylene glycol followed by a melt condensation process. The experimental details were identical with those described in an earlier publication for protonated material¹⁴. A mixture of 0.138 wt% manganese acetate and 0.042 wt% antimony trioxide was used as the catalyst.

One of the starting materials, deuterated ethylene glycol, was commercially available, whereas dimethyl terephthalate had to be synthesized. For this purpose deuterated 1,4-di-bromo-benzene was used as a starting material.

According to Gilman¹⁵ the reaction of 1,4-dibromobenzene with *n*-butyl-lithium and CO_2 yields 88% terephthalic acid. However, investigations in our laboratory showed that the crude reaction product is a mixture of terephthalic acid and 4-bromobenzoic acid:



It is not possible to reduce the amount of 4-bromobenzoic acid below 40%. This finding is in agreement with the results of other authors¹⁶⁻¹⁸ who prepared 1,4-dilithiumbenzene as an initiator of polymerization reactions.

Further investigations showed that the yield of terephthalic acid could be markedly increased by activation of the *n*-butyl-lithium with *N,N,N',N'*-tetramethyl ethylenediamine (TMEDA). The detailed procedure is described in the appendix. In this way it was possible to achieve a yield of 75% terephthalic acid and 15% 4-bromobenzoic acid.

The dimethyl ester was prepared from terephthalic acid by conversion with a commercially available BF_3 -methanol reagent under conditions described by Hallas¹⁹. The crude reaction product (yield *ca.* 95%) was twice recrystallized from methanol and distilled *in vacuo*.

The average molecular weight \bar{M} from the polymer

obtained was determined by viscometry in phenol/tetrachlorethane (3:2 weight ratio). By using the relation $[\eta] = 4.68 \times 10^{-4} \times M_w^{0.68}$ dl/g which was given by Moore²⁰. For protonated material, we obtained $[\eta] = 0.43$ which corresponds to $M_w = 23\ 000$. Gel permeation chromatography measurements were also made for both the deuterated and the hydrogenated materials before they were blended, the result indicated that their molecular weight are almost identical.

Preparation of the blends for SANS measurements

Only a few solvents exist for polyethylene terephthalate. In most solvents the polymer degrades. According to our investigations one can use either 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) which was purified in a special way¹ or nitrobenzene.

The mixtures of the deuterated and the protonated polyethylene terephthalate were prepared in the following way: The two components were dissolved in HFIP. The solvent was removed afterwards by cooling with liquid nitrogen followed by a freeze drying process.

If the pressing is performed in air, large degradation effects are observed. If, for example, the molecular weight M_w is 30 000 before pressing, it may decrease to less than 10 000 during pressing. In order to avoid any degradation heating and pressing were performed under vacuum. The sample was surrounded by a ring of silicone rubber. Immediately after the sample was situated within the ring the upper plate of the press ring was evacuated through a hole. With increasing pressure the height of the ring became smaller and the plates of the pressure reached the material and formed the film.

Table 1 shows the molecular weight M_w after pressing for 2 samples with different initial M_w , namely 35 300 and 51 700 respectively. As one can see, the sample with the lower molecular weight shows no degradation while that with the higher molecular weight is slightly degraded. As the samples for neutron scattering have a molecular weight of only 23 000 no degradation should be expected.

The samples used for SANS were melted for 3 min at 275°C with pressure of 60 bar and quenched in water to ensure that the specimens were in the amorphous state. Specimens containing 0, 50, 65, 85 and 100 wt% of the deuterated component were prepared for the SANS measurements.

SANS measurements and results

The SANS measurements were carried out at the

Institute Laue-Langevin in Grenoble. The D11 small-angle diffractometer was used. A specimen to detector distance of 10 metres, and a wavelength of 10 Å was chosen for the measurements.

After the transmission correction, a background correction was applied to the intensities of the specimens containing 50, 65, 85% DPET. The scattered intensities from the pure DPET and the pure HPET provided the base for the background subtraction. SANS data were normalized to the absolute intensity scale using water as the calibration standard. The SANS results were further normalized according to the term on the left of equation (13). The normalized absolute intensities from the specimens containing 50, 65 and 85% deuterated PET are given in Figures 1-3. The h range covered in the experiments was from 2.8×10^{-3} to 2×10^{-1} Å⁻¹ except Figure 2b where the whole scattering curve is given. The solid lines in these Figures are based on the calculation using equation (13). The term $1 + \chi(1 + h^2 a^2)^2$ in equation (13) originates from the form factor in the segregation clusters and its value tends to converge to unity rapidly in the high h region. Consequently, the value of n in equation (13) can be estimated by extrapolating the intensities at high h region to zero angle. Hereafter, the value of χ can then be determined from the extrapolated zero angle intensities using data near the minimum h region. Two more

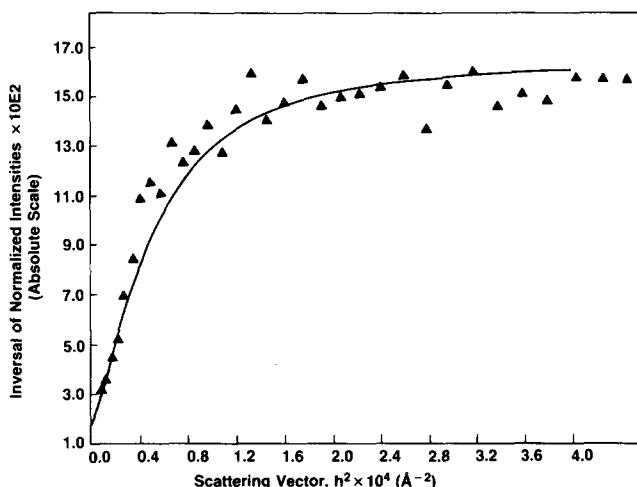


Figure 1 SANS result of 50/50 DPET/HPET blend. The experimental data are represented by (▲) and the solid line is calculated using equation (13)

Table 1 Molecular weight of poly(ethylene terephthalate) after pressing under vacuum at different temperatures T_m , for different times t_m and at different pressures P

Conditions of pressing			Molecular weight (M_w)	
Time of melting (min)	Pressure (bar)	Temperature of melt (K)	Sample initial $M_w = 35\ 300$	Sample 2 initial $M_w = 51\ 700$
3	40	548	34 600	41 100
3	40	553	32 700	40 500
3	40	558	36 100	42 500
3	60	548	32 100	40 500
3	60	553	29 500	44 500
3	60	558	36 900	43 300
5	40	548	35 400	42 600
5	40	553	36 800	43 700
5	40	558	37 100	45 800
5	60	548	35 000	43 300
5	60	553	38 400	41 300
5	60	558	41 000	48 300

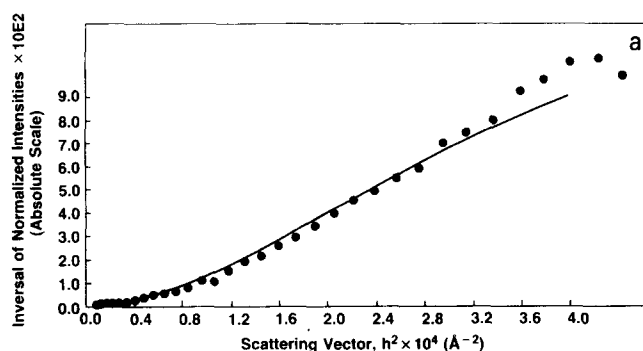


Figure 2a SANS result of 65/35 DPET/HPET blend. The experimental data are represented by (●) and the solid line is calculated using equation (13)

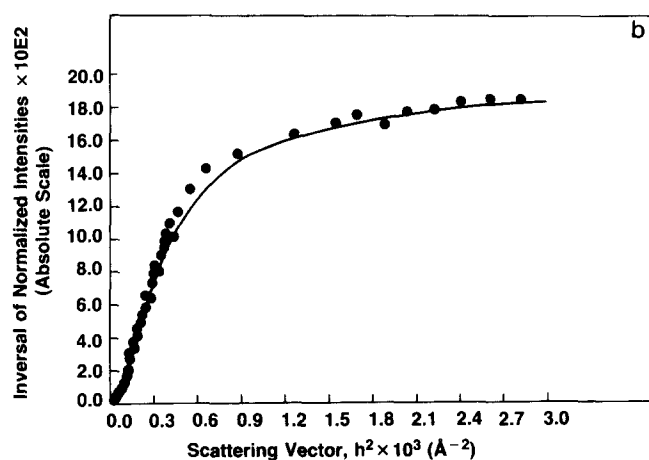


Figure 2b Same as above but in a broader scattering angle domain

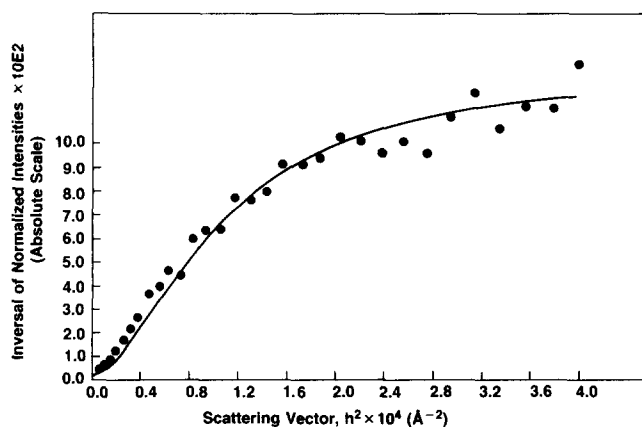


Figure 3 SANS result of 85/15 DPET/HPET blend. The experimental data are represented by (●) and the solid line is calculated using equation (13)

parameters, namely the radius of gyration R_g of blocks with molecular weight n and the correlation length a of the segregation clusters are required to be determined from the scattering data. They are estimated from a straightforward curve fitting process. The results are summarized in *Table 2*.

DISCUSSION

Independent of any scattering theories, the results shown in *Figures 1–3* clearly demonstrate a severe segregation in the amorphous DPET/HPET blends.

Table 2 The values of apparent molecular weight n (number of repeat unit), radius of gyration R_g , correlation length a of yhr clusters and the parameter χ determined from SANS

D/H ratio of PET Blend	n	R_g (Å)	a (Å)	χ
50/50	6	11	200	8
65/35	6	11	275	800
85/15	8	12	300	100

The molecular weight n calculated from the scattering data using equation (13) is only 6–8 corresponding to molecular weights lying between 1153 and 1537. These values are far below the value of 23 000 measured from the viscosity data of the SANS specimens.

These results show that during the short melting in the press transesterification processes occurred by which parts of the deuterated chains reacted with parts of the protonated chains. As a result a 'block copolymer' of the deuterated and the protonated material was formed. The 'molecular weight' of 1153 to 1537 obviously is the average molecular weight of the blocks. That such transesterification reactions occur has been deduced already by other authors under different chemical measurements¹ and follows also from changes in the molecular weight distribution during melting of mixtures of two different molecular weights observed in our laboratory².

By assuming the transesterification reactions to be a random one, the average molecular weight of the blocks is expected to increase as the composition of the specimens is deviated from 50/50 in terms of DPET and HPET ratio. This trend is indeed observed in this work as shown in *Table 2*. The correlation length a of the segregation clusters is expected to change with the D/H composition in the same fashion as for the values of n . Again, this trend is observed from the values of a presented in *Table 2*.

The values of R_g in *Table 2* were obtained from a curve fitting process using equation (13). The calculated values of R_g based on a degree of polymerization of 6 to 8 is between 13 and 15 Å²¹. They are fairly close to those evaluated from the SANS measurements.

The value of χ defined in equation (11) is proportional to the composition difference of these two domains as well as to the product $\phi(1-\phi)$, where ϕ is the volume of one domain. The large difference in the values of χ shown in *Table 2* indicates that one of the quantities or both depend strongly on some experimental details specimen preparations which were not controlled.

Equation (13) is originally derived for blends of two homopolymers of equal molecular weight. This equation can be applied to block copolymers only if there is no correlation between the blocks of each species, that is a random block copolymer. We believe that the transesterification process between these DPET and HPET chains will result in a random block copolymer. Hence, the use of equation 13 to treat the present SANS data is believed to be correct for the 50/50 blend where the D and H blocks have the same molecular weight. As to the other blends of unequal parts, equation (13) is not strictly applicable due to the difference in the block lengths of the D and H species. However, values of R_g and the theoretical results tends to support the applicability of equation (13) even to those cases.

It is noteworthy that there are four independent

parameters in equation (13) to be determined from every single scattering curve; these four parameters are n , R_g , χ and a . In treating the partially segregated blends, the two phase models adopted in the present work is believed to be a highly simplified one. Even so, this treatment yields four parameters in the final expression. From the scattering curve, what can be determined unequivocally is the multiple $n\chi$ from the zero angle extrapolation. Based on equation (13) and the scattering curves, the values of n , R_g and a are deduced from the curve fitting process. The reason that so many parameters can be deduced from a single scattering curve is due to certain characteristics inherent in equation (13); the h region over which the intensities rise sharply is dominated by the value of a , and the slope and the height of the intensities at the high h region are dictated by n and R_g . Accordingly, values of n , χ , R_g and a presented in Table 2 are sensitive to the model on which equation (13) is based. Furthermore, certain simplifications have also been used in the derivative of equation (13), e.g., equation (8) is a good approximation in the case of a monodisperse molecular weight; in the present case the size distribution of the H or D blocks is surely not monodisperse. Accordingly, equation (8) may well be an oversimplification for the present case. Therefore equation (13) might later be shown to be inadequate to treat the PET case described herein due to its complexity. However, any modification of the current two phase model is likely to yield an expression with more than four parameters, hence the advantage for further modifications is not apparent.

CONCLUSION

With the method developed it becomes possible to evaluate small-angle neutron scattering experiments also in the case of segregation of the deuterated material. The considerable segregation observed seems to be no longer a serious problem in the determination of the resulting radius of gyration and the molecular weight. This opens the possibility of investigating such materials as poly(ethylene terephthalate) where it is difficult to avoid segregation.

In further experiments we intend to change systematically the melting conditions and to study the influence of these changes on the transesterification. Another aim of future investigations will be to find melting conditions under which the transesterification effect is as small as possible, so that the change of radius of gyration of the chains upon crystallization and orientation of the material can be examined. Also, the influence of the preparation conditions on the segregation could then be determined.

ACKNOWLEDGEMENTS

We would like to thank Professor E. W. Fisher for many instructive discussions on the SANS scattering theory. We are also indebted to the Bundesministerium für Forschung und Technology (BMFT) for financial support of this work.

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APPENDIX: SYNTHESIS OF THE TEREPHTHALIC ACID

77 ml (0.509 mole) N,N,N',N' -tetramethyl ethylenediamine are placed in a three-necked flask purged with argon. The flask is cooled to 278 K. A solution of 0.509 mole *n*-butyl-lithium in 200 ml pentane is added. After 20 min of complexation time one begins to add a solution of 30 g (0.125 mole) 1,4-dibromobenzene in 500 ml pentane through a dropping funnel as quickly as possible so that the temperature in the flask does not exceed 293 K. 3 h later the flask is cooled with dry ice/ethanol to 238 K and powdered dry ice is added to the solution. When the temperature reaches about 268 K one adds 200 ml 1 N NaOH. The two phases are separated and the pentane phase is twice extracted with 150 ml portions of 1 N NaOH. The NaOH phases are acidified with 6 N HCl. The white precipitate thus obtained is collected on a Buchner funnel, washed several times with water and dried at 100°C *in vacuo*. The yield is 90%. Investigations by mass spectrometry showed that the material remained fully deuterated.