Macromolecules 1987, 20, 1116–1119

Study of Transesterification in Poly(ethylene terephthalate) by Small-Angle Neutron Scattering

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Received April 22, 1986

ABSTRACT: Small-angle neutron scattering (SANS) experiments were carried out on blends of deuteriated and nondeuteriated poly(ethylene terephthalate) (PET). The scattering results obtained for blends that had been prepared by melt-pressing at different temperatures for different lengths of time indicated that transesterification had occurred during pressing, resulting in the formation of a block copolymer consisting of labeled and nonlabeled segments of PET. The decrease in both the molecular weight and the radius of gyration of these blocks with time is presented. A method is developed to calculate the block size after the transesterification process. The time and temperature dependence of the block size established that the transesterification is an Arrhenius type reaction. The occurrence of considerable molecular exchange is shown which may explain the unique crystallization behavior in PET samples that have been annealed for several weeks above the normal crystallization temperature. Finally, the values obtained for the ratio of the radius of gyration to the square root of the molecular weight are in good agreement with those previously obtained for the PET system in solution under Θ-conditions.

Introduction

Through the use of deuterium labeling, small-angle neutron scattering (SANS) has been found to be an extremely effective tool for elucidating the structure of polymer molecules in the condensed matter state. Most SANS studies that have been performed to date have been performed on polymers of a noncondensation type, e.g., polyethylene, polystyrene, polypropylene, etc., with which interchain interactions can be avoided during the blending and melt pressing of bulk samples. When polymers prepared by condensation polymerization are investigated by SANS, the presence of interchain interactions between the nondeuteriated and deuteriated molecules (such as transesterification with poly(ethylene terephthalate)) must also be considered or in some way avoided to correctly interpret the scattering results obtained. In the neutron scattering study conducted by McAlea[1] et al., transesterification was avoided by initially solvent casting films of poly(ethylene terephthalate) (PET) and then pressing at a low temperature for several minutes. The samples obtained in this way were semicrystalline. By a somewhat different procedure, namely, precipitation from solution followed by melt pressing for 20 s at 250 °C, we were able to obtain amorphous samples and to study the change of radius of gyration caused by crystallization and by drawing of the polymer.[2]

Since understanding the kinetics of transesterification in PET during melt processing is of great industrial interest, in this work, we use small-angle neutron scattering (SANS) to investigate the influence of temperature and time on the amount of transesterification. Amorphous blends of deuteriated and nondeuteriated PET are annealed for different times at 280, 275, and 250 °C. During this annealing, by transesterification, molecules consisting of blocks of deuteriated and nondeuteriated chains are formed. After this, the molecular weights and the radii of gyration of the blocks are obtained by SANS.

Experimental Section

Poly(ethylene terephthalate) (PET) was synthesized in both its deuteriated and nondeuteriated forms from ethylene glycol and dimethyl terephthalate as described in a previous publication.[3] As catalysts, 0.138 wt % manganese acetate and 0.042 wt % Sb_2O_3 were used. Deuteriated and nondeuteriated PET were then blended by codissolving them in hexafluoro-2-propanol followed by reprecipitation in a methanol nonsolvent. The precipitate was then dried in a vacuum oven, melt-pressed under vacuum at 280, 275, or 250 °C, and quenched in ice water to prevent crystallization, yielding a clear polymer film. According to SAXS investigations and density measurements the samples were completely amorphous. As a result of the transesterification occurring during the melt-pressing process, the H and D polymer molecules were transformed into H–D block copolymers. The block molecular weight and its radius of gyration are then obtainable from the neutron scattering profile.

The neutron scattering experiments were performed at the ILL in Grenoble using the D11 diffractometer with a sample-to-detector distance l of 5 m and a neutron wavelength λ of 10 Å and with the D17 spectrometer with $l = 2.8$ m and $\lambda = 12$ Å.[4,5] The wavelength resolution (fwhh) $\Delta\lambda/\lambda$ was 9% (D11) and 10% (D17), respectively. The data were collected on a 64 × 64 two-dimensional position-sensitive detector.

Data Evaluation

At first the two-dimensional data are circular averaged by ILL-supported routines[6] to obtain the one-dimensional scattering curve $I(q)$, with $q = (4\pi/\lambda)\sin(\theta/2)$ being the scattering vector. After subtraction of the empty cell the resulting intensity was divided by the transmission factor and sample volume.[6] Normalization to an absolute intensity scale was done with 1-mm pathlength of water as the standard, which scatters nearly incoherent and isotropic.[7] Inelastic and multiple scattering effects of the 1-mm water standard are corrected by an empirical calibration factor $g(\lambda)$ resulting from investigations on samples with well-known molecular properties.[8] Incoherent and coherent background are subtracted according to Gawrisch et al.[9,10] to get the reduced intensity $I(q)$. Hayashi et al.[11]

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propose a different subtraction of the incoherent background. But as the samples we used have high transmission rates, greater than 80%, the method of Hayashi et al. would lead to similar results.

Finally $I(q)$ is divided by the contrast $(a_H - a_D)^2$ of the monomer unit and its number density per unit volume S_N

$$I(q) = S_N(a_H - a_D)^2 S(q) \tag{1}$$

For the presentation of the results this normalized scattering intensity $S(q)$ is used.

Theory

With the random-phase approximation (RPA) theory applied on a system composed of independent protonated and deuteriated chains with a degree of polymerization of Z_H and Z_D, respectively, and assuming that the Flory interaction parameter $\chi_{H/D}$ is zero,[12-14] one obtains

$$S^{-1}(q) = \frac{1}{xZ_D P(q)} + \frac{1}{(1-x)Z_H P(q)} = \frac{1}{x(1-x)Z_{SANS} P(q)} \tag{2}$$

with the single-chain structure factor $P(q)$ given by

$$P(q) = 1 - q^2 R_g^2/3 + ... \tag{3}$$

Z_{SANS} is the degree of polymerization as determined by small-angle neutron scattering. In the case of polydisperse systems the weight average of Z_{SANS} and the z average of R_g are obtained.[15]

In the system investigated in this work two or more tagged blocks are connected to a H–D block copolymer, caused by the transesterification. The scattering intensity of such a melt can also be evaluated with the RPA theory.[16,17] Considering a sample with all chains partly tagged and each chain having the *same* sequence of tags, de Gennes[12] predicted a "correlation hole" effect: At $q = 0$ the scattering intensity starts at zero, increasing to a peak and decreasing at larger q values essentially like independent scatterers (tagged portions of the chain). Leibler and Benoit[18] calculated the scattering curve in the RPA for a di- and triblock copolymer. In the case of a constant block length they got the same scattering behavior as de Gennes with a peak at $qR_g \approx 2$. Additionally they introduced a distribution of the block lengths with a polydispersity $M_w/M_n \geq 1$ as the parameter. They showed that from monodisperse to polydisperse systems the peak in the scattering curve shifted to smaller q values with greater polydispersity and additionally the intensity at $q = 0$ increased. Finally they got a monotonically descending curve at $M_w/M_n = 2$: The chemical polydispersity cancels the correlation hole effect, a behavior measured qualitatively by Benoit et al.[19]

Hong and Noolandi,[20] who objected somewhat to the derivations of Leibler and Benoit, derived an expression for the scattering curve of a block copolymer having a Schultz–Flory distribution. Under the assumption of such a distribution with a polydispersity $M_w/M_n = 2$ and $\chi_{H/D} = 0$, it can be shown that the inverse scattering intensity $S^{-1}(q)$ approximates to

$$S^{-1}(q) = \frac{1}{x(1-x)Z_{SANS}}(1 + q^2R_g^2/3)$$

for $1 < x(1-x)q^2R_g^2$, which is identical with the scattering curve of a mixture of independent H and D labeled molecules.

The correlation between chemical connected blocks could be seen only as a deviation at scattering vectors smaller than $q^2 \approx 1/R_g^2$, in which region we did not perform the evaluation.

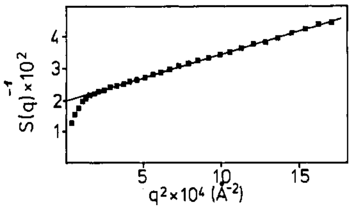

Figure 1. Zimm plot of noncrystalline PET blend (50% PETD) melt pressed at 280 °C for 10 s and quenched. $S(q)$ is given in absolute intensity.

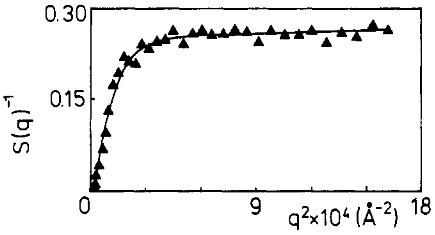

Figure 2. Zimm plot of a noncrystalline PET blend (10% PETD) melt pressed at 280 °C for 180 s and quenched. $S(q)$ is given in absolute intensity.

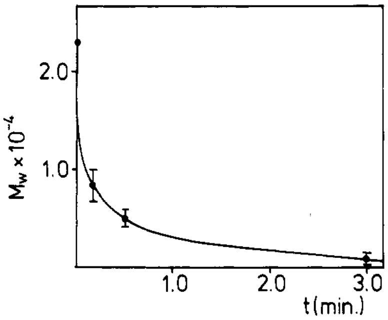

Figure 3. Average block molecular weight M_w for PET blends vs. melting time t at 280 °C.

Results and Discussion

Molecular Weight and Radius of Gyration of the Blocks. SANS results were obtained from samples melt pressed for different lengths of time at 280 °C. A first qualitative sight of the scattering curves gave no hints for a correlation hole effect. In the Zimm representation the scattering curves follow a linear behavior (Figure 1). Only at small q values do the samples annealed for 180 s show an *additional* scattering and not *a diminution* as expected from RPA theory in the case of uniform blocks (Figure 2). A similar additional scattering intensity was found[3] for another sample annealed for the same time at 275 °C. In that publication a more extensive data analysis was carried out, in which the possibility of phase separation of the H- and D-tagged blocks was allowed.

To simplify data evaluation in the asymptotic region ($qR_g > 2$), the labeled blocks are regarded as independent scatterers. With a Zimm plot of the data (Figures 1 and 2) the block molecular weight was determined from the extrapolated value of the neutron scattering intensity at zero q and the block radius of gyration is determined (Table I) from the ratio of the slope to the intercept. Inclusion of the scattering data down to $qR_g > 1$ leads to identical results.

The speed with which transesterification takes place during melt pressing at 280 °C is easily observed in the graphical presentation of the average decrease in the SANS-determined molecular weight as a function of the annealing time in Figure 3. In an earlier publication[3] it was observed by light scattering (LS), GPC, and viscometry that no decrease in molecular weight of the polymer molecule itself occurred due to degradation for PET of M_w

Table I
Block Molecular Weight M_w, z Average of the Radius of Gyration, R_{gz}, Ratio $(R_{gw}^2/M_w)^{1/2}$, and Number, u, of Intermolecular Reactions per Molecule as a Function of Pressing Time at 280 °C

pressing time, s	compn, % PETD:% PETH	M_w	$(R_{gz}^2)^{1/2}$, nm	$(R_{gw}^2/M_w)^{1/2}$, nm mol$^{1/2}$/g$^{1/2}$	u	$\bar{u}$
10	50:50	9900	4.6	0.038	2.6	
	30:70	7600	3.5	0.033	3.5	3.0 ± 0.7
	70:30	7300	3.8	0.036	3.7	
	10:90	8200	3.6	0.032	2.2	
30	50:50	5600	3.4	0.037	6.2	
	30:70	4200	2.8	0.035	7.7	6.8 ± 0.8
	70:30	4900	3.1	0.036	6.4	
	10:90	5600	3.5	0.038	3.8	
180	70:30	940	1.6	0.044	40	
	10:90	780	1.4	0.040	35	37.5 ± 3.5

Table II
Radius of Gyration of the Samples Annealed for 180 s Compared to That of a Corresponding Rod

compn	Z	$(R_{gw}^2)^{1/2}_{\text{sample}}$, nm	$(R_g^2)^{1/2}_{\text{rod}}$, nm
70:30	4.7	1.4	1.5
10:90	3.9	1.2	1.2

= 35 300 at 285 °C. Therefore, no degradation should be expected for blend samples in the study with M_w = 23 000. Nevertheless, the block length in H–D blends is drastically reduced to less than half its original value in 10 s at 280 °C; for 20 s at 250 °C a 45 000 molecular weight PET blend was reduced to 27 000 (approximately 60% of its original value). After a pressing time of 3 min at 280 °C, the 23 000 molecular weight PET has an average block molecular weight of only approximately 900.

Let us discuss now the values of radii of gyration. We consider first the samples pressed for 10 and 30 s. An average value of 0.043 nm was obtained from the data in Table I for the ratio of the z-average radius of gyration to the square root of the molecular weight. In another publication[2] we show that the PET scattering data can be described by assuming a Schulz–Flory distribution with a polydispersity M_w/M_n = 2, which is reasonable for polycondensation polymers. Then with the procedure of Greschner[21] the z-average radius of gyration can be converted to its weight average, and a value of 0.036 nm is then obtained for the above ratio. This is only slightly lower than the value predicted by Flory[22] of 0.0394 nm and in excellent agreement with the value obtained experimentally by McAlea et al.[1] of 0.0373 nm.

For the sample pressed for 180 s, $R_{gw}/M_w^{1/2}$ is larger than expected. Therefore, in Table II, the z-average radii of gyration of annealed samples are changed to the weight-average radii and compared to the value calculated for a rod having Z times the length of a monomer unit. For the 10:90 blend with blocks of 4 monomer units the radius of gyration is identical with that of a rod. For the 70:30 blend with larger blocks (Z = 4.7), the radius of gyration lies between that of a rod and that of an equivalent Gaussian coil (1.1 nm). Here one can see the beginning of the coiling due to the fact that there is already some flexibility within the chain.

Kinetics of Transesterification. Let us consider the kinetics of transesterification in order to calculate the influence of the fraction x of deuteriated material on the block lengths obtained. As the chemical attack is independent of the position along the chain, it is reasonable to assume a Schulz–Flory distribution of the blocks with a polydispersity $(M_w/M_n)_{\text{block}}$ = 2 identical with that of the total chain.[23,24] The number of times each molecule has undergone transesterification is called u.

In order for the occurrence of chain transfer by transesterification to have any effect on the scattering, two unlike chains must exchange segments. Thus the factor by which the block molecular weight is decreased for a given molecule is not $1/(u + 1)$ as it would be if all chain-transfer reactions were profitable but is $1/[u(1 - x) + 1]$ for deuteriated segments and $1/(ux + 1)$ for nondeuteriated segments, under the assumption of identical reaction velocities for both materials.

Thus the values for Z_H and Z_D for a given blend can be calculated in terms of the weight average of the original degree of polymerization Z_{LS} measured by light scattering (LS) and the number of intermolecular reactions per molecule that have occurred, u, and one obtains from eq 2

$$\frac{1}{S(q)} = \left[xZ_{LS}\left(\frac{1}{u(1-x)} + 1\right)\right]^{-1} + \left[(1-x)Z_{LS}\left(\frac{1}{ux+1}\right)\right]^{-1}\frac{1}{P(q)} \tag{4}$$

$$\frac{1}{S(q)} = \frac{(1-x)^2u + (1-x) + x^2u + x}{x(1-x)Z_{LS}}\,\frac{1}{P(q)} \tag{5}$$

Since we want the ratio of Z_{SANS} to Z_{LS} as a function of x and u, we substitute according to eq 2 and 3 and consider the value $q = 0$ only

$$S(q = 0) = x(1-x)Z_{SANS} \tag{6}$$

Z_{SANS} being the weight-average degree of polymerization observed by SANS which corresponds to the average degree of polymerization of the blocks.

Thus eq 5 becomes

$$Z_{SANS} = r_e Z_{LS} \tag{7}$$

where

$$r_e = \frac{1}{1 + (x^2 + (1-x)^2)u} \tag{8}$$

Since r_e is a function of x, the H–D PET blends of different compositions should appear to have different blocks sizes for the same annealing time. Nevertheless, the number of transesterifications per molecule u should be constant. Equation 8 can be rearranged to give

$$u = \frac{(1/r_e) - 1}{x^2 + (1-x)^2} \tag{9}$$

For each blend u was calculated (Table I). It is constant for the samples annealed for 180 and 30 s, respectively.[26] The films annealed the shortest time (10 s) exhibit stronger deviations, which might be explained by the difficulty in preparing these samples reproduciably.

For each annealing time an average number $\bar{u}$ of transesterifications per molecule was evaluated (see Table I) and plotted as a function of the transesterification time

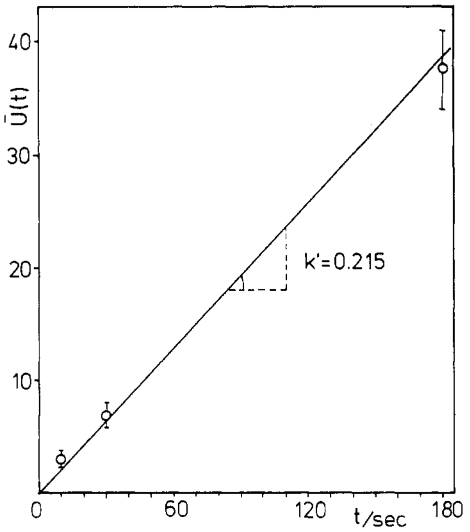

Figure 4. Number of transesterifications per molecule at 280 °C as a function of transesterification time t.

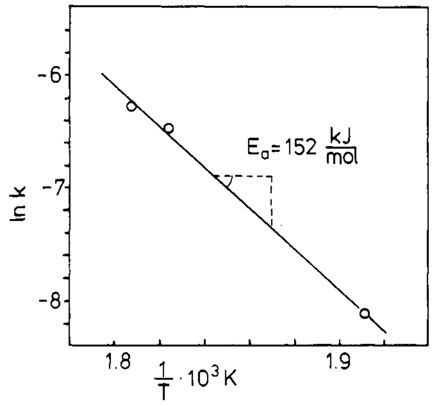

Figure 5. Arrhenius plot of the transesterification rate constant k.

t (Figure 4). It can be seen that $\bar{u}$ increases linearly with time

$$\bar{u} = k't \tag{10}$$

where

$$k' = 0.215 \text{ s}^{-1} \tag{11}$$

In the same manner, the rate constants k' of two other sample sets annealed for 180 s at 275 °C and for 20 s at 250 °C were evaluated. Comparison of these results obtained from samples with different molecular weights was made by normalizing the rate constants k' by the degree of polymerization Z to give the rate constants k per monomer unit (Table III).

$$k = k'/Z \tag{12}$$

An Arrhenius representation of these constants ($\ln k(T)$ vs. T^{-1}, Figure 5) shows a linear dependence yielding an activation energy of E_a = 152 kJ/mol.

Conclusions

With interchange reactions taking place to such a great extent in PET, these reactions should not be ignored when considering the mechanisms of processes occurring in the melt, such as crystallization or lamellar thickening. Interchain reactions such as transesterification could pose as possible mechanisms for decreasing the number of entanglements in the interlamellar regions and increasing the number of the chains between lamellae. Thus the occurrence of transesterification in PET is a likely explanation of the unique ability of PET to form high-density crystals when annealed for several months at 290 °C, a temperature normally considered to lie above T_m.[25]

Table III
Transesterification Rate Constants Per Molecule (k') and Per Monomer Unit (k) as a Function of Temperature

T, K	k', s	$k \times 10^3$, s
553	0.215	1.87
548	0.178	1.55
523	0.067	0.30

Acknowledgment. We thank Dr. S. Bantle for valuable discussions and experimental assistance and Dr. P. Lindner for his help in preparing the manuscript. The SANS facilities were kindly provided by the Institute Laue-Langevin, Grenoble, France. This work has been funded by the German Federal Minister for Research and Technology (BMFT) under Contract No. 03-ZA1HAM-3.

Registry No. PET, 25038-59-9; neutron, 12586-31-1.

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