Structural Investigations of Segmented Block Copolymers. II. The Morphology of Poly(ether Ester)s Based on Poly(tetramethylene Oxide) "Soft" Segments: Comparison between Poly(ether Ester)s and Poly(ether Esteramide)s

G. PEREGO, M. CESARI, and R. VITALI, *Assoreni, Physical Chemistry Department, 20097 San Donato Milanese, Milano, Italy*

Synopsis

The morphology of poly(ether ester)s (PEES) of the general formula $[(4GT)_k\text{-PTMO}]_z$ has been investigated by wide and small angle X-ray scattering and electron microscopy techniques. The copolymers are based on poly(tetramethylene terephthalate) (4GT) "hard" segments (containing an average number k of consecutive 4GT units) alternating poly(tetramethylene oxide) (PTMO) "soft" segments of constant length (MW $\sim$ 900). The fraction of crystallized 4GT slightly increases by increasing the weight fraction of PTMO up to ca. 0.5; then it rapidly decreases so that an amorphous material is obtained for a PTMO weight fraction of 0.76. PEES display a lamellar-type morphology in which lamellar domains of crystalline 4GT alternate with slightly heterogeneous interlamellar amorphous regions containing both 4GT and PTMO. For high contents of PTMO these domains evolve toward amorphous domains formed by short 4GT segments ($k = 2, 3$). PEES and the structurally related poly(ether esteramide)s are compared in terms of their morphological structure.

INTRODUCTION

The recent commercial introduction of thermoplastic elastomers has stimulated considerable interest both in the synthesis and in the study of the peculiar morphology of this unusual materials.

Poly(ether esteramide)s (PEEA), based on poly(esteramide) "hard" segments and poly(tetramethylene oxide) "soft" segments, are new segmented block copolymers belonging to this class, which have been synthesized in our laboratories.[1] An intensive research program has been carried out, concerning the structure, morphology, and properties of these copolymers.[1-4] Moreover, it was felt of interest to investigate parallely other copolymers like poly(ether ester)s (PEES), based on poly(tetramethylene terephthalate) "hard" segments and the same poly(ether) "soft" segments of PEEA.

Previously, Cella,[5] Shen et al.,[6] Seymour et al.,[7] and Lilaonitkul et al.[8] have given a general picture of the morphology of PEES, which accounts for the lamellar-type structure as well as for the spherulitic superstructure of these copolymers; however, the models proposed for the lamellar organization are not conclusive. The subject has been faced in more recent papers by Wegner et al.,[9-11] in which interesting results, obtained mainly by application of SAXS, DSC, and electron microscopy techniques are reported. Nevertheless, some of the conclusions drawn by the authors seem to us questionable.

CCC 0021-8995/84/041157-13$04.00

In a previous paper the detailed results of the investigation on PEEA have been reported, and a quantitative description of the morphology of these materials has been given.[4] In this paper we report the results of the investigation on PEES, obtained by the application of the same techniques (mainly WAXS, SAXS, and electron microscopy) and procedures used for PEEA. Moreover, a comparison between the two series of copolymers is given, in terms of their morphological structure.
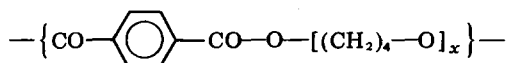
DEFINITION OF THE MACROMOLECULAR STRUCTURE

PEES are conventionally defined[12] by the general notation
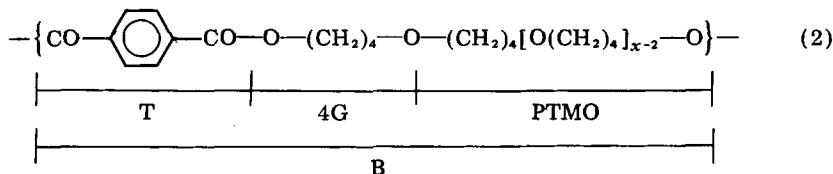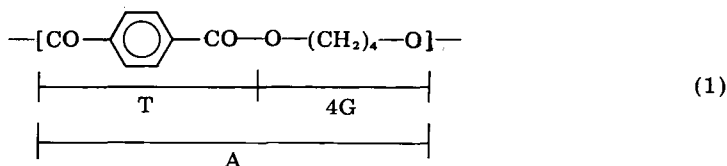
$$(A_m B_n)_z$$

where the "hard" A and "soft" B units are

$$-[CO-\langle\bigcirc\rangle-CO-O-(CH_2)_4-O]-$$

and

$$-\{CO-\langle\bigcirc\rangle-CO-O-[(CH_2)_4-O]_x\}-$$
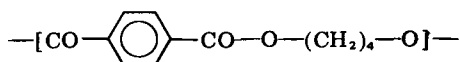
respectively. m, n, z, and x have the same meaning, previously indicated for PEEA.[4]

As for PEEA, let us rewrite A and B units with proper subunits:

$$-[CO-\langle\bigcirc\rangle-CO-O-(CH_2)_4-O]- \tag{1}$$

$$\underbrace{}_{T} \underbrace{}_{4G}$$
$$\underbrace{}_{A}$$

$$-\{CO-\langle\bigcirc\rangle-CO-O-(CH_2)_4-O-(CH_2)_4[O(CH_2)_4]_{x-2}-O\}- \tag{2}$$

$$\underbrace{}_{T} \underbrace{}_{4G} \underbrace{}_{PTMO}$$
$$\underbrace{}_{B}$$

Applying the same arguments as for PEEA and substituting the T-4G with the more familiar 4GT labeling, it can be verified that the chain of PEES is formed by sequences of 4GT units separated from each other by the poly(ether) PTMO unit specified in (2). Therefore, the general notation

$$[(4GT)_k - PTMO]_z \tag{3}$$

may be assumed, k representing the average number of consecutive 4GT units. The extreme compositional limits are the poly(tetramethylene terephthalate), $(4GT)_z$, and the alternate configuration $(4GT-PTMO)_z$, respectively. As for PEEA, the notation

$$(H_k - S)_z \tag{4}$$

will be used for sake of clarity, the symbols H and S indicating the "hard" 4GT and the "soft" PTMO units, respectively.

EXPERIMENTAL

Materials. Samples of PEES have been synthesized following a procedure similar to the one described for PEEA[1]; poly(tetramethylene ether)glycol (PTMEG) with a number average molecular weight of 1000 has been used, as for PEEA. The composition of the copolymers, following both the conventional and the new descriptions, was derived as for PEEA[4]; the molecular weights of A, M_A, and B, M_B, units for PEES are 220.2 and 1130.1, respectively. According to formula (4), the weight fraction of 4GT segments, w_H, can range from 0.20 (k = 1) to 1.0 (4GT homopolymer); the corresponding maximum content of PTMO, w_S^{max}, is 0.80. The investigated samples, with w_S in the range 0–0.76, are identified by the label "PEES" followed by the weight percent of PTMO units. A commercial sample of poly(tetramethylene terephthalate) (Ultradur, BASF) was used; it has been labeled as PEES-0. As for PEEA, the composition of the copolymers, determined by NMR analysis,[13] is in good agreement with the one expected on the basis of the composition of the reaction mixture.

Specimens compression molded with the same procedure described for PEEA[4] were used. The density of the samples was measured by conventional density gradient technique.

A list of the samples investigated is reported in Table I.

Techniques. Wide angle (WAXS) and small angle (SAXS) X-ray scattering measurements as well as transmission electron microscopy (TEM) observations were performed, as described in detail for PEEA.[4] TEM experiments were also carried out on samples in the form of thin films, cast from a solution of the polymer in 1,1,2,2-tetrachloroethane.

Procedures. The details concerning the procedures followed in the calculation of crystallinity, w_c, and electron density variance $\overline{\eta^2}$ have been previously reported.[4]

RESULTS AND DISCUSSION

Crystallinity

The crystal phase typical of poly(tetramethylene terephthalate), α-form,[14,15] is clearly detected in WAXS patterns of PEES, some of which are reported in Figure 1. No crystallization of PTMO was observed in any case.

As a general trend, the crystalline weight fraction, w_c, decreases with the increase of the weight fraction of PTMO units, w_S; the slope is steeper for $w_S >$ 0.45 and a completely "amorphous" material is obtained for very high w_S (PEES-76). As found for PEEA, the values of w_c obtained from the experimental overall density [by eq. (11), Ref. 4] are systematically higher than those drawn from WAXS measurements. However, the differences between the two sets of values are much smaller than for PEEA, so that the regression curve fitting all experimental values [see Fig. 2(a)] may be considered a fairly good estimation of crystallinity. As in the case of PEEA, the slight excess of crystallinity from density may be accounted for by some organization of a part of hard segments

TABLE I
Sample Description and Experimental Data

Sample	ρ^a (g·cm^{-3})	$w_A{}^b$	$w_H{}^c$	$w_{H(k)}{}^d$ $k=1$	2	3	>3	$w_c{}^e$ WAXS	Density	Extrap.	L (Å)		$10^3\,\overline{\eta^2}$ [h]	σ^2 (Å^2)[i]
PEES-0	1.322	1.0	1.0					0.42		0.42	122^f	105^g	1.25	0
PEES-13	1.269	0.84	0.87	<0.01	<0.01	<0.01	0.86	0.39	0.40	0.39	151	125	3.37	0
PEES-15	1.259	0.81	0.85	<0.01	<0.01	<0.01	0.84	0.37	0.39	0.39	155	124	3.49	2.1
PEES-27	1.214	0.67	0.73	<0.01	<0.01	0.01	0.71	0.31	0.34	0.35	157	123	4.28	1.7
PEES-31	1.200	0.62	0.69	0.01	0.02	0.02	0.64	0.30	0.35	0.34	157	123	4.60	0
PEES-33	1.196	0.59	0.67	0.01	0.02	0.02	0.62	0.31	0.36	0.34	158	126	4.70	2.7
PEES-43	1.161	0.47	0.57	0.02	0.03	0.04	0.48	0.27	0.33	0.29	162	130	5.04	1.5
PEES-56	1.113	0.31	0.44	0.04	0.05	0.06	0.29	0.20	0.25	0.21	190	140	4.55	0.6
PEES-62	1.088	0.23	0.38	0.06	0.07	0.07	0.18	0.12	0.17	0.15	200	145	3.22	0
PEES-71	1.058	0.12	0.29	0.10	0.08	0.05	0.06	0.03	0.10	0.07	225	190	1.65	2.5
PEES-76	1.039	0.05	0.24	0.15	0.06	0.02	0.01	0	0	0	230	190	0.65	5.3

a Mass density, exptl values.
b Weight fraction of A units, conventional description; see text.
c Weight fraction of 4GT units, actual description, see text.
d Weight fractions of 4GT sequences containing k 4GT units, calculated according to Ref. 17 for infinite chain length.
e Crystalline weight fraction.
f Long spacing from desmeared SAXS curves.
g Long spacing from desmeared and Lorentz corrected SAXS curves.
h Electron density variance, in (mol-electrons)^2 cm^{-6}, from SAXS.
i Variance of the interface thickness following Ruland; see Ref. 4.
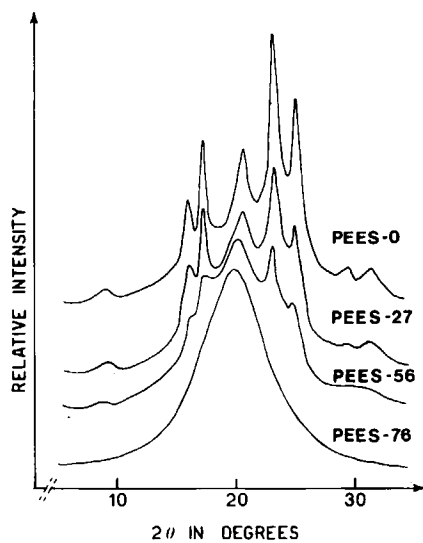
Fig. 1. Smooth traces of WAXS patterns of poly(tetramethylene terephthalate) (PEES-0) and typical poly(ether ester)s.
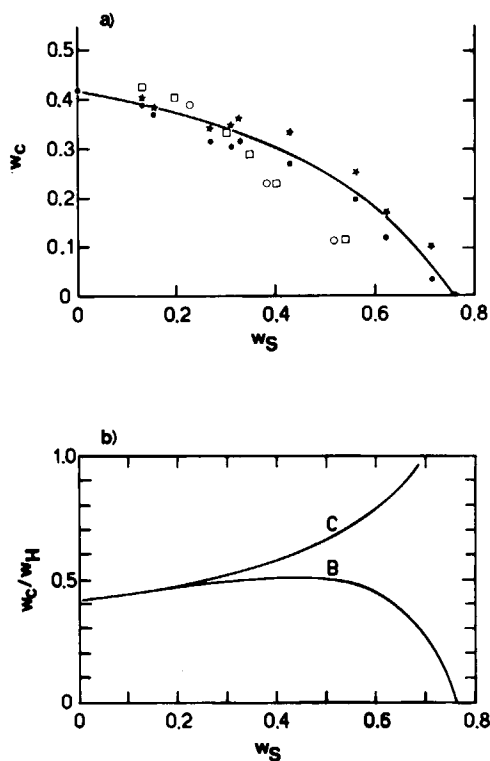

Fig. 2. (a) Crystallinity in poly(ether ester)s: from density ($\star$); from WAXS ($\bullet$); from DSC, Refs. 8 ($\square$) and 9 ($\bigcirc$). (b) Fraction of crystallized 4GT, w_c/w_H (curve B) and $w_c/w_{H(>3)}$ (curve C), vs. the weight fraction of PTMO.
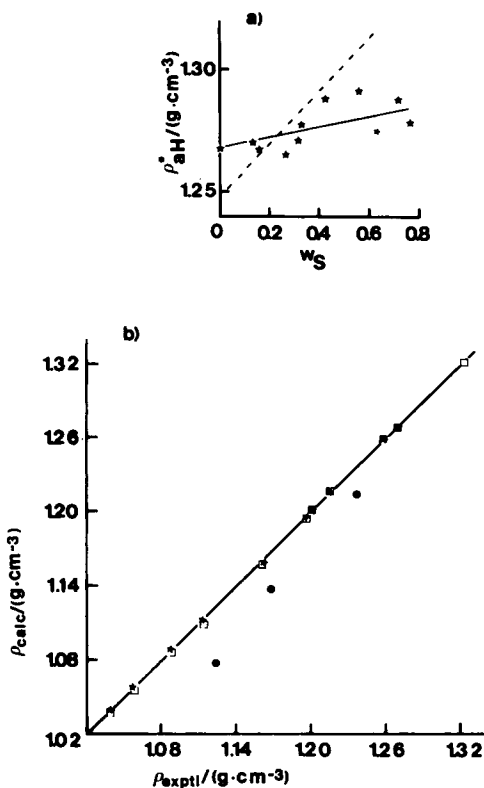
Fig. 3. (a) Mass density of amorphous 4GT, ρ^*_{aH} [from eq. (11), Ref. 4], vs. the weight fraction of PTMO. Dashed line represents the trend in poly(ether esteramide)s. (b) Calculated overall density [by eq. (11), Ref. 4] from ρ_{aH} ($\square$) and ρ^*_{aH} ($\star$) vs. experimental overall density. Calculated and experimental values from Ref. 9 ($\bullet$).

in pseudoamorphous domains. By using the w_c from the above regression curve and the experimental values of the overall density, the density of "amorphous" 4GT, ρ^*_{aH}, may be calculated [by eq. (11), Ref. 4] as the function of w_S. The plot of Figure 3(a), in spite of the scattering of the points, shows a linear increase of ρ^*_{aH} with w_S; however, the slope is markedly lower with respect to PEEA, indicating that only slight ordering phenomena occur in "amorphous" 4GT.

The fraction of crystallized 4GT, w_c/w_H [see Fig. 2(b), curve B], slightly increases up to $w_S \sim 0.5$; the decrease observed above this value is due to the progressive increase of the amount of uncrystallizable short 4GT segments. It must be remarked that the complete disappearance of crystallinity (PEES-76) practically coincides with the lack of 4GT sequences having more than three 4GT units, H(>3); see Table I. If the $w_c/w_{H(>3)}$ ratio is used, the curve C [Fig. 2(b)] is obtained, which displays a trend quite similar to the one observed for PEEA. When considering the results shown in Figure 2(b), we cannot agree with the statement of Wegner et al.[9] "in PEES, sequences shorter or longer than the average sequence length do not crystallize."

In Figure 2(a) the values of the crystallinity, obtained for PEES by Lilaonitkul et al.[8] and Wegner et al.[9] by DSC measurements, are reported after reduction of the sample compositions to our description: these results are consistent with
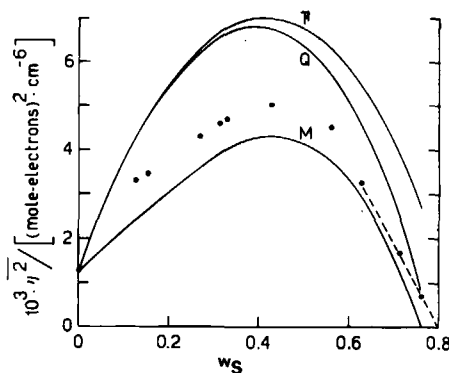
Fig. 4. Experimental (●) and calculated (two-phase, curve M, and three-phase, curves T and Q, structures) values of the electron density variance vs. the weight fraction of PTMO.

ours for low w_S, but lower than ours for high w_S, i.e., in the region of lower crystallinity. This is not surprising, because enthalpy of fusion is generally rather depressed by both point defects and surface effects, which become more important with the decreasing of crystallinity. On the other hand, lower w_c values have been obtained also for PEEA, by application of DSC technique.[1] Taking into account the volumetric meaning we give to crystallinity, the results reported in the present paper should be considered more correct.

Nature of the "Amorphous" Fraction

As for PEEA, the electron density variance $\overline{\eta^2}$, measured by SAXS method, has been taken into account in order to achieve informations about the structure of the so called "amorphous" fraction. Inspection of Figure 4 shows that the experimental $\overline{\eta^2}$ values, after the attainment of a maximum for $w_S \sim 0.45$, decrease steeply by a further increase of w_S: a linear extrapolation of the last three points leads to $\overline{\eta^2} = 0$ for $w_S^{max} = 0.80$, i.e., for the alternate $(H\text{–}S)_z$ configuration. This does indicate that isolated 4GT units are not able to segregate but by far prefer to dissolve in the amorphous PTMO phase. In the same Figure 4, the experimental values of $\overline{\eta^2}$ are compared with those calculated by a procedure previously described,[4] relative to different structural models. For the sake of clarity, the calculated values of $\overline{\eta^2}$ have been reported in form of curves, instead of discrete points, after a smoothing procedure has been applied. All the values used in calculating $\overline{\eta^2}$ (see Table II) fit the experimental values of the overall density; the same fitting is not displayed by the data reported by Wegner et al.[9] [see Fig. 3(b)].

The models considered in the calculation of $\overline{\eta^2}$ are: a two-phase model formed by a crystalline 4GT phase and an amorphous phase arising from homogeneous mixing of the remaining fraction of 4GT and PTMO (curve M); two three-phase models, one where amorphous PTMO and uncrystallized 4GT are segregated (curve T), the other where all the isolated 4GT units are homogeneously mixed with PTMO (curve Q).

By excluding the copolymers with high w_S, the experimental $\overline{\eta^2}$ values are generally closer to the curve of the two-phase model than to those of the three-phase ones; this indicates a tendency towards a homogeneous amorphous structure, though the presence of some heterogeneity has to be admitted. This
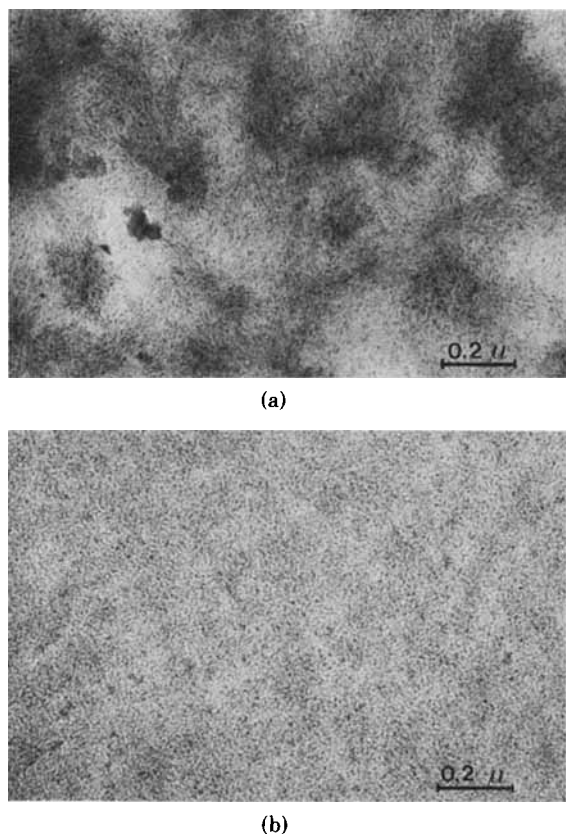
Fig. 5. Transmission electron micrographs of solvent cast films of PEES-31 (a) and PEES-56 (b) samples.

last conclusion agrees with the evidence of slight ordering phenomena in the amorphous fraction (see the previous paragraph). When considering the highest PTMO contents, one can remark that the extreme value of the curve Q (w_S = 0.76) is almost coincident with the corresponding experimental point, indicating a tendency to phase segregation for this copolymer composition. Because we noted above that isolated 4GT units mix homogeneously with PTMO and no segment with more than three 4GT units is available (see Table I), phase segregation must involve segments with 2–3 units; however, the domains formed by these segments never reach paracrystalline order; therefore they do not give rise to diffraction lines in WAXS patterns.

Morphological Organization of the Phases

Both TEM and SAXS investigations on PEES confirmed the previous conclusions for a lamellar-type morphology[5–11] over the entire composition range investigated. TEM micrographs (see Fig. 5) show lamellar-type domains, generally less extended with respect to PEEA series[4]; thin films allow a better visualization of the morphological structure than thin sections, in agreement with previous results.[5,10]
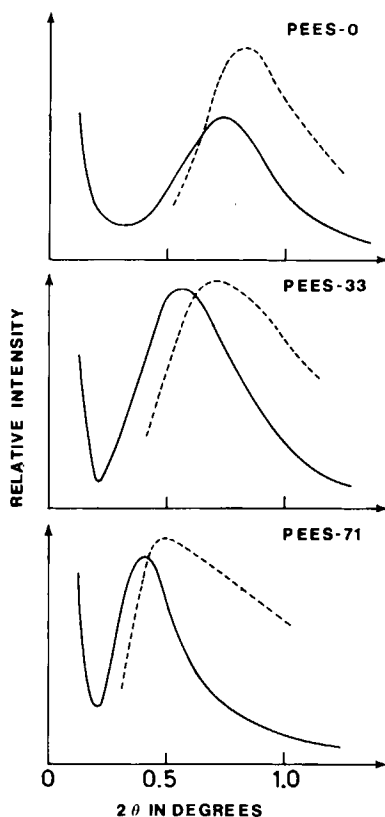
Fig. 6. SAXS patterns of poly(tetramethylene terephthalate) (PEES-0) and typical poly(ether ester)s; desmeared (——) and desmeared and Lorentz corrected (- - -) curves.

A well-defined SAXS peak is detected for the whole composition range (see Fig. 6). The corresponding "long spacing" L, derived from both simply desmeared and desmeared and Lorentz corrected SAXS curves (this feature has been discussed in Ref. 4), is reported in Table I. As well evidenced in Figure 7, the systematic differences between the two sets of L values do not prevent drawing the trend of L as a function of the copolymer composition. L slightly increases with respect to the PEES-0 homopolymer, remaining approximately constant up to w_S 0.5; a further increase of w_S results in a quite steep increase of L. It is worth noting that a SAXS peak is observed also for the completely amorphous sample PEES-76.

The values of L reported by Wegner et al.[9] for three different PEES copolymers (w_S in the range 0.2–0.5), quenched or slightly annealed, agree satisfactorily with the corresponding ones reported in the present paper.

In the range of low and medium w_S values, lamellar domains are built up of crystalline 4GT segments while a transition to "amorphous" lamellar-type domains (formed by uncrystallizable short 4GT segments) is observed for high values of w_S, in agreement with the arguments already discussed. This transition should occur gradually through the formation of less and less ordered micro-paracrystals.
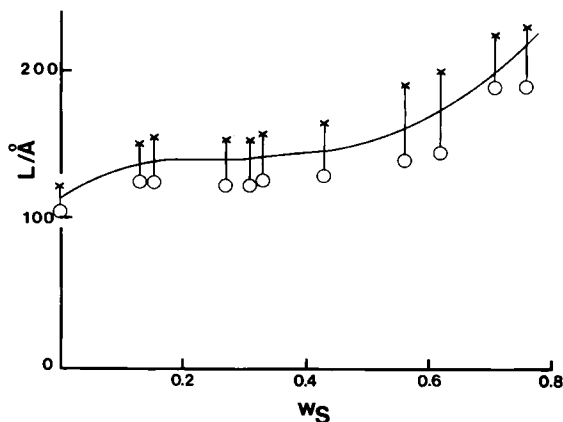
Fig. 7. Long spacing, L, from desmeared (X) and desmeared and Lorentz corrected SAXS curves (O), vs. the weight fraction of PTMO.

By assuming the lamellar structure to be volume filling, the average thickness of the lamellar domains, l_c is related to L by $l_c = L \cdot \varphi_c$, where φ_c is the crystalline volume fraction easily obtained by w_c. In the w_S range 0–0.5, where L is nearly constant, l_c slightly decreases from 40–50 to 30–40 Å, depending on whether L is derived from desmeared or desmeared and Lorentz-corrected SAXS curve; these values correspond approximately to 4–5 and 3–4 4GT units, re-spectively. [The length of a 4GT unit in the crystal state, projected perpendicularly to the lamella surface is 9.7 Å (d_{001}).[14,15]] For higher values of w_S, φ_c cannot be exactly derived, owing to the presence of amorphous lamellar domains; however, it is reasonable to assume that l_c tends to a minimum value of 20–30 Å corresponding to "amorphous" lamellar domains containing 4GT segments with 2–3 units (see above). The increase of L for $w_S > 0.5$ must therefore arise from an increase of the interlamellar average thickness, $l_a = L - l_c$. Evidently, this is the consequence of the increased interlamellar volume fraction or, in other words, of the decreased φ_c, due to the decreasing availability of 4GT segments capable for segregation (H > 1); in PEES-76 the total volume fraction of these segments is less than 10%. Moreover, for this last reason, it may be inferred that the lamellar-type structure is not volume-filling for the highest PTMO contents.

The detection of a sharp SAXS peak for the whole composition range suggests that the lamellar domains mostly maintain a fairly good alignment in the macrolattice; probably, this is favored by the low degree of heterogeneity existing in the interlamellar regions (see the preceeding paragraph). In PEEA, these regions are highly heterogeneous and SAXS peaks disappear for a given composition range.[4]

COMPARISON BETWEEN THE MORPHOLOGIES OF POLY(ETHER ESTER)S AND POLY(ETHER ESTERAMIDE)S

The existence of a macrolattice containing crystalline, lamellar in shape domains is clearly demonstrated over the entire composition range in both PEEA and PEES, the lateral extension of these domains generally decreasing by in-

creasing the content of soft segments. However, our results do not allow us to get an insight into the structural feature concerning the extent of chain folding occurring in the lamellar-type domains. As far as PEES are concerned, opposite views exist for this feature in the literature: chain folding occurs largely in the model of Seymour et al.,[7] but only occasionally in the model of Wegner et al.[9-11]

In our opinion, in both PEEA and PEES, real lamellae with a relatively large amount of chain folding exist in copolymers with low soft content, being the crystallizing 6NT6 (or 4GT) segments markedly longer than the average thickness of the lamellar domains formed.

When increasing the soft content, a continuous evolution from real lamellae towards a smectic-like, lamellar in shape, arrangements of microparacrystals occurs. At the same time, the average length of the crystallizing segments is reduced, becoming of the order of the lamellar thickness. In this case, the probability that folding occurs should be reduced, each folding having to involve at least one, relatively long PTMO segment. In this view, the extent of chain folding decreases by decreasing the average sequence length of 6NT6 (or 4GT) sequences, in other words, by increasing the PTMO content. It is probable that when approaching the composition limit of the alternate $(H-S)_z$ configuration, the occurrence of chain folding is really occasional.

The main features of the morphology of the two series of copolymers can be accounted for by some of their molecular or thermodynamical characteristics such as the length of the "hard" unit, the segmental incompatibility, the chain flexibility and the block-length distribution. In PEEA, the fraction of crystallized hard segments increases with the increase of the concentration of PTMO soft segments, w_S, reaching unity by approaching w_S^{max}. On the contrary, completely amorphous PEES are obtained near to the same composition limit. The length of the "hard" unit is mainly responsible of these behaviors. In fact, the considerable length (ca. 30 Å) of the 6NT6 unit assures in PEEA an intrinsic crystallization ability even of the isolated units; on the contrary, the short length (ca. 10 Å) of the 4GT unit does not allow crystallization of short 4GT segments, in particular of those containing less than four 4GT units.

Segmental incompatibility is higher in PEEA than in PEES as indicated by the higher difference between the solubility parameters (calculated according to Ref. 16) of 6NT6, 11.9 $(cal\cdot cm^{-3})^{1/2}$, and PTMO, 8.6 $(cal\cdot cm^{-3})^{1/2}$ than between the same parameters of 4GT, 9.6 $(cal\cdot cm^{-3})^{1/2}$, and PTMO. Segmental incompatibility accounts for the larger extent of phase segregation between "hard" and "soft" segments observed in the amorphous part of PEEA with respect to PEES.

Because chain flexibility depends largely on the "soft" component, the role played by it should be nearly the same in both copolymers. In fact, crystallization of the "hard" segments is favored in both series by an increasing chain flexibility; accordingly, the fraction of crystallized "hard" segments increases with w_S in a similar way both in PEEA and PEES, provided the "crystallizable" segments only (those with $k > 3$ in PEES) are considered.

Block length distribution concerns the "hard" segments only, being the length of the "soft" segment practically uniform in both copolymers. The fact that the distribution becomes sharper and sharper when approaching the composition of the regularly alternate $(H-S)_z$ configuration certainly contributes to the

TABLE II
Values of the Mass Densities ($g \cdot cm^{-3}$) Used in the Calculation of $\overline{\eta^2}$

$\rho_{cH} = 1.405$	(average between 1.404^a and 1.406^b)
$\rho_{aH} = 1.268^c$	
$\rho_{aS} = 0.981$	(average among $0.98,^d$ $0.981,^e$ and 0.983^f)
$\rho_{aH}^* = 1.268 + 0.021w_S{}^g$	

^{a,b} From structural X-ray analysis, Refs. 15 and 14, respectively.

^{c} From exptl values of density and $\overline{\eta^2}$; see Procedures in Ref. 4.

^{d} Ref. 16.

^{e,f} From exptl values of $\overline{\eta^2}$ of PTMEG 1000 and 2000 MW, respectively; see Procedures in Ref. 4.

^{g} From the regression in Figure 3(a).

complete phase segregation (crystalline lamellar-type domains of 6NT6 alternating amorphous PTMO) observed in PEEA with high w_S. On the other hand, a similar influence is evident also in PEES with w_S close to w_S^{max}, the 4GT segments (with $k > 1$) being almost completely segregated in amorphous domains. However, the role played by the block length distribution remains secondary, if one consider that, in PEES, the alternate $(H-S)_z$ copolymer displays an homogeneous amorphous structure, in spite of the regularity of its chain configuration.

REMARKS

Finally, it is worth doing some remarks about the annealing behavior of these copolymers, starting from the results reported for PEES by Wegner et al.[9] These authors have shown an exponential increase of long spacing as well as a sharpening of the melting endotherm in copolymers (with w_S in the range 0.2–0.5), annealed near their melting point. They conclude that "domains of hard segments of a certain length are formed by quenching and that only the fraction of these domains and their perfection changes on annealing." Though we agree with the increase of perfection and size of the crystals, we think that crystallization near the melting point involves preferentially the longest 4GT sequences; shorter 4GT sequences, able to crystallize at lower temperatures, should remain amorphous, so enlarging the interlamellar region and, consequently, the long spacing. Evidently, the thickening of the lamellar crystals can also contribute to the increase of long spacing, but this contribution should be important mainly in copolymers with low soft content, when longer 4GT sequences are available.

In this view, a slight decrease (at least no increase) of the amount of crystallized 4GT is to be expected when PEES are annealed near their melting points. Therefore, the increase of the melting enthalpy on annealing, observed by the above-mentioned authors, should arise essentially from the improved perfection of the crystals.

As expected, a few qualitative annealing experiments indicate a similar trends for PEEA with low and medium content of soft segments, but a quite different behavior is observed for copolymers with elevated soft content. In fact, no significant variation of crystallinity as well as of long spacing was observed after annealing at 150°C the PEEA-59 sample (mostly constituted by chain segments

with alternate $(H-S)_z$ configuration (see Table I in Ref. 4), in agreement with the fact that an almost complete crystallization of 6NT6 already exists before annealing. Clearly, when approaching the composition of the alternate $(H-S)_z$ copolymer, the relatively high regularity of the chain configuration and the high intrinsic incompatibility between PTMO and 6NT6 units, can lead only to the above described morphology, independently of the thermal history.

References

1. E. Sorta and G. della Fortuna, *Polymer*, **21**, 728 (1980).

2. G. della Fortuna, A. Melis, G. Perego, R. Vitali, and L. Zotteri, Proceedings of the International Rubber Conference, Venice, 1979, p. 229.

3. A. Biggi, G. della Fortuna, G. Perego, and L. Zotteri, *Kautsch. Gummi, Kunstst.*, **34**, 349 (1981).

4. G. Perego, M. Cesari, G. della Fortuna, *J. Appl. Polym. Sci.*, **29**, 1141–1155 (1984).

5. R. J. Cella, *J. Polym. Sci., Polym. Symp.*, **42**, 727 (1973).

6. M. Shen, U. Mehra, M. Niinomi, J. T. Koberstein, and S. L. Cooper, *J. Appl. Phys.*, **45**, 4182 (1974).

7. R. W. Seymour, J. R. Overton, and S. L. Corley, *Macromolecules*, **8**, 331 (1975).

8. A. Lilaonitkul, J. C. West, and S. L. Cooper, *J. Macromol. Sci. Phys.*, **812**, 563 (1976).

9. G. Wegner, T. Fujii, W. Meyer, and G. Lieser, *Angew. Makromol. Chem.*, **74**, 295 (1978).

10. Li-Lan Zhu and G. Wegner, *Makromol. Chem.*, **182**, 3625 (1981).

11. Li-Lan Zhu, G. Wegner, and U. Bandara, *Makromol. Chem.*, **182**, 3651 (1981).

12. W. H. Buck, R. J. Cella, Jr., E. K. Gladding, and J. R. Wolfe, Jr., *J. Polym. Sci., Polym. Symp.*, **48**, 47 (1974).

13. C. Corno, unpublished results.

14. Z. Mencik, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 2173 (1975).

15. M. Yokouci, Y. Sakakibara, Y. Chatani, H. Tadokoro, T. Tanaka, and K. Yoda, *Macromolecules*, **9**, 266 (1976).

16. D. W. Van Krevelen, *Properties of Polymers. Correlations with Chemical Structure*, Elsevier, New York, 1972.

17. E. Sorta and A. Melis, *Polymer*, **19**, 1153 (1978).