Styrene and Polystyrene Modified Polyethylenes: Characterization and Properties

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STYRENE AND POLYSTYRENE MODIFIED POLYETHYLENES: CHARACTERIZATION AND PROPERTIES

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ABSTRACT

The initial structures of thin polyethylene films and of thin slices obtained from thicker specimens crystallized at temperature gradient in the modification process by styrene and polystyrene are studied. Comparison of the structures of these two types of samples shows clearly that the initial morphology and lamellar structure of the matrix has a basic influence on the modification process.

INTRODUCTION

Swelling-induced crystallization in glassy and amorphous polymers has been reported in several papers. Diffusion of liquid or gaseous penetrants takes place in the entire volume of these polymer materials. In partially crystalline polymers, where the crystalline elements behave like unpermeable units, diffusion of penetrating molecules is limited not only in those elements with a relatively high crystalline perfection but also in partially ordered regions of polymers [transition layers (lamellae surface layer), smectic phase, etc.]. Such "paracrystalline" regions are shown to be particularly sensitive to the swelling and reordering processes.

Swollen polymer can partially recrystallize in processes in which the

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intensity depends on the respective solubilities of the swelling agents and the experimental conditions (temperature, swelling time period). Consequently, such a swelling-induced modification can be used as an alternative method for the structure reorganization which is usually realized in solid crystalline polymers by heat treatment. The above method should be very useful in the case of polymers which degrade when thermally treated or undergo undesirable structural changes.

The concept of structure–properties modification with styrene (ST) as an intensively penetrating liquid was experimentally verified for a low density polyethylene (LDPE) in our recent works [1–4]. ST can be used as a modifying agent in two ways. After swelling at various diffusion conditions, it can be separated from the LDPE matrix by evaporations. Thus, the structure of the initial film is modified to a large extent. On the other hand, ST can be polymerized *in situ* in LDPE, e.g., by UV irradiation. The final specimen has the characteristics of a structure modified both by the swelling procedure and by the presence of polystyrene (PS).

It has been shown that the structure of PE–PS systems depends on the modification conditions: the temperature of diffusion (T_D) and the time period of ST diffusion into the PE matrix. The most evident structural effects observed in the PE–PS system are connected with matrix reorganization, while the two-component constitution of the system only weakly influences its mechanical properties.

A deep reorganization of the structure of this polymer has been observed as a result of styrene treatment. Structural reordering is reflected in a high differentiation of permeation and viscoelastic properties after such a modification. The extent of ST diffusion into LDPE films depends on their internal structure. The specific, partially crystalline structure of LDPE has been discussed by many authors [5–11] who have suggested several models of the crystalline phase containing crystalline lamellae with various stabilities at different temperatures. It is accepted that crystalline elements of higher stability crystallize from the melt in the form of chain-folded lamellae. The chains included have chain segments much longer than the fold period. The chains with shorter unperturbed segments can take part in the crystallization of less stable elements whose thickness is determined by the length of the segments and by the thermal conditions of preparation. They melt at distinctly lower temperatures than the melting point. During annealing, lamellae can recrystallize to form more perfect crystalline elements [12, 13].

Since diffusing ST swells the amorphous phase of PE, decomposes

the crystalline elements characteristic of lower stability, and also extracts ·a low molecular weight LDPE, the mobility of the macromolecules in the decomposed material is relatively high. When the penetrant is removed in the evaporation process, recrystallization in the matrix occurs (swelling-induced crystallization). The structural changes observed are similar to the annealing effects at T_D; however, the lamellae formed are of higher perfection and stability. Evidently all the structural changes in the crystalline and amorphous phases induced by the swelling agent and fixed by the polymerization of ST depend on the initial structure of the LDPE matrix and on the conditions of LDPE–PS system preparation.

The present investigation shows some aspects of the relationship between the initial structure of LDPE and the modifications which result from ST treatment and/or from the presence of PS. These structural changes have been studied by DSC, small- and wide-angle x-ray scattering, and dynamic mechanical measurements carried out using samples with different initial structures. We also want to take into consideration the results obtained for thin slices obtained from thicker modified samples. The initial structure of those specimens has been modified by crystallization in a temperature gradient [14].

EXPERIMENTAL

Sample Preparation

The details of sample preparation were described in previous papers (see, e.g., Refs. 2–4, 14). Thus, we will present only a brief compilation here. Thin spherulitic films of LDPE (1800S-BASF), 0.4 mm thick, were obtained by crystallization from the melt between two metallic plates at 0°C. Two films prepared in the same way were placed in liquid ST at 65°C for 2 h. One of the samples was subsequently irradiated by UV light for 3 h in order to initiate polymerization of ST and to obtain a two-component system (PE–PS) (P samples). The second film was removed from the ST bath and dried in vacuum for 48 h (N samples). All samples were stored at 20°C for 1 month before examination.

Thick LDPE films (~9 mm) were obtained by hot pressing circular plates between two metallic blocks at 90 and −70°C, respectively. Crystallization was completed in 1 h.

A solidified sample was placed in a chamber with liquid ST and diffusion was carried out at 65°C for 4 h. Monomer penetrating into the

sample through the surface produced a gradient ST content in its successive layers. This preparation technique made it possible to obtain samples with an ST gradient in the direction of decreasing crystallinity (penetration through the sample surface crystallized at 90°C). The second sample (the flux of ST) had the opposite result (diffusion through the surface crystallized at −70°C).

A second class of samples containing PS was obtained by UV irradiation after swelling with ST. The thick samples were sectioned (Reichert-Jung microtome) parallel to the surface of the discus-like specimen (perpendicular to the gradients of PS or ST-treated samples without ST, or perpendicular to the structure gradient created by crystallization at the temperature gradient). Thin sections are identified by the numbers 1 to 9 to indicate the different initial structures and the various structural modifications by ST treatment or by the presence of PS.

All these samples were examined by using selected techniques for structure and properties characterization.

Experimental Methods

The supermolecular structures of the initial LDPE as well as of the N and P samples and sectioned layers were determined by small-angle light-scattering patterns (SALS).

The degree of crystallinity was calculated from wide-angle x-ray scattering. Crystallinity was correlated with the results of SAXS. Long spacing values of the lamellar structure have been determined from $I(s)s^2$ scattering plots by application of the desmearing procedure elaborated by Strobl [13]. Reorganization of the structure of the crystalline phase of polyethylene has been analyzed on the basis of DSC thermograms (Metler TA 3000) at a heating rate of 10 K/min. The PS content was determined from the absorption intensity measurements of the characteristic PS peak at 269 nm. The mechanical properties were investigated in the 10^{-2} to 10^2 Hz frequency range by dynamic tension experiments.

RESULTS AND DISCUSSION

Comparison of the structure and properties of thin ST-modified PE films and PE–PS specimens with thin sectioned layers leads to some interesting conclusions. The structure of the PE matrix depends on both the supermolecular structure and on the lamellar structures resulting

TABLE 1.Morphological Characteristics of Modified N and P Samples (thin films)

Sample	Average spherulite radius R, μm^a	Perfection factor η	Degree of crystallinity, %
PE	4.6	0.63	0.38
N	4.3	0.7	0.46
P(16 wt% of PS)	4.8	0.49	0.38

[a]Values of R calculated from the maxima of SALS.

from temperatures of initial sample preparation and of subsequent treatment. Thin films of initial spherulites with different average radii and similar perfection factors are modified by ST to a different extent. The perfection factor η is defined

$$\eta = \frac{\int_0 I_s(d\theta)}{\int_0 I_{tot}d\theta}$$

where $I_s(d\theta)$ is the SALS scattering intensity for $\mu = 0°$ and $I_{tot}(d\theta)$ is the SALS intensity for $\mu = 45°$ [4]. By using this method it was found that for thin films with larger initial spherulites, the resulting morphological structure was more disturbed by ST penetration (samples N after ST evaporation). However, it must be pointed out that only small differences in PS (after polymerization of ST) contents were found for such films with various spherulite sizes. Thus, the amount of PS included after polymerization cannot be responsible for the above-mentioned modification efficiency. At high temperatures, ST diffusion occurs not only in interspherulitic regions, but also to a large extent in the spherulitic structures. Extraction of the low molecular weight fraction of polyethylene leads to higher structural reorganization. In the case of PS-containing films, the spherulitic structure is reorganized in a similar way only in the first stage of modification; namely, during styrene diffusion. Polymerization of ST hinders reorientation of the crystalline elements in the spherulites. The initial order of crystalline elements is strongly disturbed when the sample reaches the swollen state, and then it is fixed by the polymerizing styrene. Some data characterizing the morphology of ST-modified and PS-containing thin films are collected in Table 1.

Comparison of the structure and properties of thin sections of thick LDPE specimens crystallized in a temperature gradient revealed some
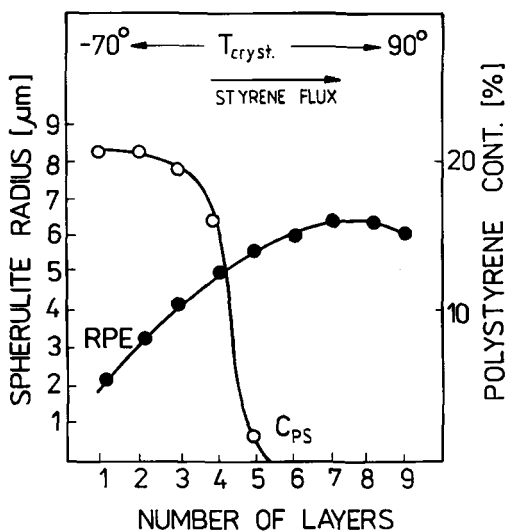
FIG. 1. Spherulite radius RPE in PE matrix polystyrene content dependence on styrene flux in sample crystallized in temperature gradient −70°C → +90°C.

similarities and some differences. Styrene penetration depends on the direction of its flux from the "cool" side containing small spherulites or from the "hot" side containing bigger spherulites. These diffusion conditions at constant T_D result in different penetration depths of ST and, consequently, in a different distribution of PS following polymerization. In the first case, because of smaller spherulites in the surface layer, ST penetration into PE is less hindered, but penetration is deeper in the thick specimens (at given crystallization conditions in a temperature gradient). Penetration drops rapidly; thus, in the 6th thin slice, ST concentration is very small as is the amount of PS. A different PS concentration distribution is observed when the PS flux first penetrates the "hot" side with its bigger spherulites. ST diffusion is somehow limited, but due to the partial reorganization of the structure, ST penetrates deeply into the thick sample. The decrease of PS concentration is small and reaches its highest value in the 3rd layer (see Figs. 1 and 2). This clearly shows that the initial morphology has an important influence on structural modification and PS content. These results are complementary
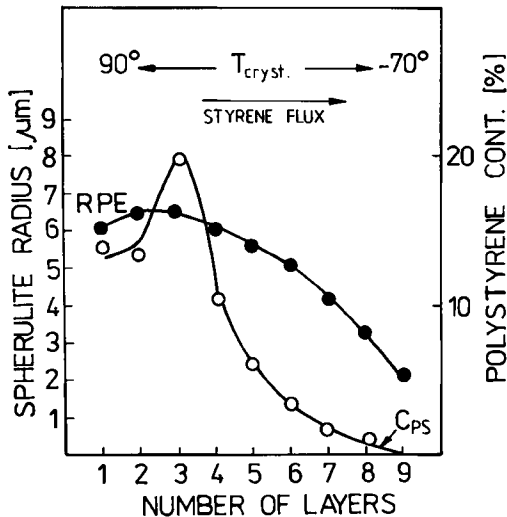
FIG. 2. Spherulite radius RPE in PE matrix and polystyrene content dependence on styrene flux in sample crystallized in temperature gradient $+90°C \rightarrow -70°C$.

to those obtained for thin films in which a clear variation of morphology through the film thickness is difficult to achieve.

Interesting conclusions on the influence of crystallinity can also be reached from investigations of thin slices. The crystallinity of PE increases with increasing temperature inside thick specimens. This is easily understood by taking into consideration the kinetics of crystallization. Crystallinity reaches 32% for the 1st layer at the "cool" surface and 42% at the "hot" surface. The presence of ST leads to an increase of crystallinity because of swelling-induced crystallization. The polymerization of ST, however, does not result in full fixation of the structural rearrangement taking place during ST diffusion. This effect is made particularly clear by considering the long spacing values L determined by SAXS. The increase of L values is seen by comparing the LDPE matrix, for which $L = 9.2$ nm, with the ST-modified slices (N) as well as PS containing thin sections for which $L = 11$ and 10.7 nm, respectively. The lamellae in P slices are slightly thinner. This result is confirmed by DSC thermograms (melting temperatures). The details of these studies are described in a previous paper [14].
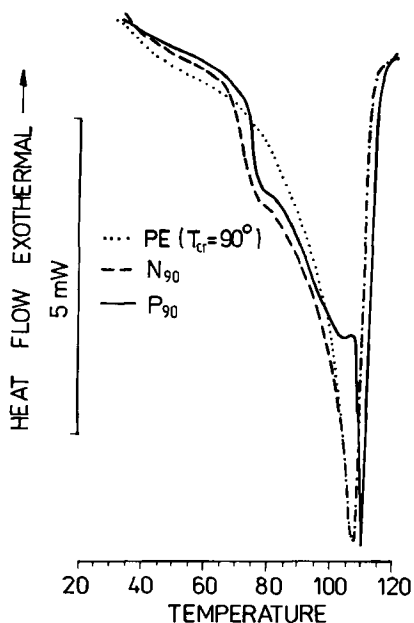
FIG. 3. DSC thermograms obtained for thin PE film crystallized at 0°C.

We want to show here the DSC traces characteristic of the highest crystallinity obtained for the 3rd layer. Treatment with ST or the presence of ST results in a differentiation of lamellar thickness (melting temperatures) (Fig. 3) and a shift to higher temperatures connected with an increase of lamellar thickness and stability of lower perfection in the initial sample. The presence of PS causes some restriction in lamellae thickness distribution (two clear shoulders and a sharp melting point for the most perfect crystalline elements). Comparison with DSC thermograms for thin films (Fig. 4) crystallized at 0°C reveals that ST-treatment (N) films and polymerization of ST results in less pronounced changes of melting temperatures (compare with Fig. 3). The lower initial crystallinity degree and the smaller, less perfect morphological structures result in some differentiation of structural elements.

The results of studies of dynamic mechanical properties confirm the different behavior of thin PE films formed at 0°C and thin slices of material crystallized at the temperature gradient. Comparison of thin films and slices can be made in two ways: By considering slices close to
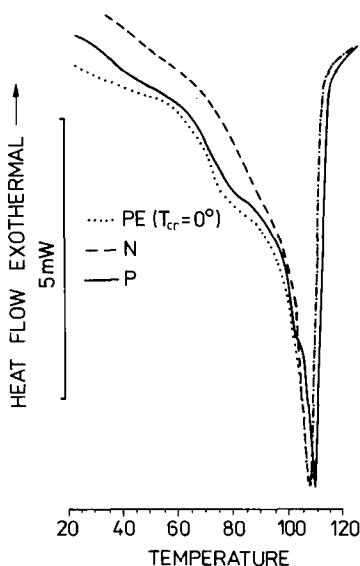
FIG. 4. DSC thermograms obtained for Slice 3 from sample crystallized at temperature gradient $+90°C \rightarrow -70°C$.

the "cool" side or the mostly crystalline specimen. The structure of thin films is generally more similar to that of thin slices close to the "cool" surface. The decomposition of the initial structure during ST diffusion and evaporation results in an increase of, and the appearance of, a clear maximum of loss factor (see Figs. 1b and 3b in Ref. 4 and Fig. 10 in Ref. 14). The similarities of the frequency dependence of the moduli are clear. A different behavior is shown by the 3rd slice prepared in the temperature gradient starting from the "hot" side. The continuous increase of modulus M' and of tg δ (Fig. 5) is seen (without a tg δ maximum). This is due to high crystallinity, to higher perfection of the initial lamellae, and to a lower extent of recrystallization induced by swelling. The penetration of ST causes stiffening of the inter- and intralamellar amorphous phases related to stretching of the chain elements connecting the crystalline grains. After polymerization of ST, the structure becomes harder, resulting in a higher modulus and a lower intensity of internal relaxation processes.
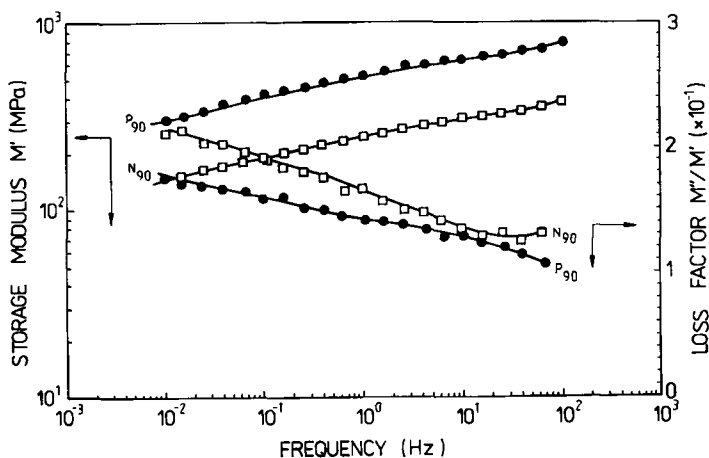
FIG. 5. Storage modulus M' and loss factor M''/M for Slice 3 modified with styrene (N) and polystyrene (P).

CONCLUSIONS

Modification of the initial structure of PE by ST treatment and/or by the presence of PS depends to a large extent on the initial structure of the matrix. The structural characteristics of the slices obtained from thicker specimens of PE crystallized in a temperature gradient confirm this result directly.

The slices corresponding to a low temperature of crystallization are basically modified by penetrating styrene in analogy to thin films (swelling-induced crystallization).

Slices corresponding to crystallization at a high temperature (and particularly the 3rd layer) are only slightly modified during recrystallization induced by styrene. The structural modifications are mainly governed by the presence of PS inclusions in the amorphous phase. When PS is included close to the amorphous phases (interfacial regions of lamellae), it makes the system stiffer due to driving the tie molecules in these interfacial or interlamellar regions to a more stretched state.

We can now reach some conclusions about the similarities and differences between thermal annealing and modification by ST or PS. The main difference is connected with the thermal stability of lamellae formed in both processes. Annealing at a given temperature results in

melting of those lamellae which are thinner and, consequently, an increase of thicker lamellae. Liquid styrene is less selective in that respect, but the strong interacting molecules of ST monomer separate the crystalline grains in the lamellae independently on their initial thickness. Thus, modification of PE by this monomer is more extensive and can be controlled to a large degree by the swelling conditions and the initial structure of PE.

The structural modifications induced by styrene are not limited to PE but can also be used for other polyolefins, e.g., isotactic polypropylene. In any case, thin films are characteristic of crystalline forms with various perfections and stabilities. Thus, their modification can also result in transformation between different ordered forms (particularly the smectic phase). Our recent studies [15] showed that transition layer thickness between ordered, amorphous, and/or smectic phases can be ascribed to swelling-induced reordering in these regions. High perfection of the crystalline phase makes the crystalline elements more stable, and modifications occur particularly in the transition layers in the vicinity of the lamellae. This is in some contrast with LDPE in which the modifications occur by destruction of the thinner crystalline elements and the formation of new lamellae [16].

ACKNOWLEDGMENTS

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