Correlation Between Microstructure and Physical Properties in Styrene–Ethylene Copolymers

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SYNOPSIS

The structural organization and the physical properties of a new copolymer styrene–ethylene have been analyzed. The composition was 80% of ethylene units, corresponding to 52% in weight, with a distribution of styrene units in the chain implying the absence of styrene–styrene sequences. The length of the polyethylene chains, limited by the insertion of the phenyl group, is not sufficient to allow good crystallization, and in fact the copolymer shows a very low crystallinity, of the order of 5–10%, and a broad melting range, with a peak centered at 120°C. The small crystalline domains are segregated into an amorphous matrix, producing a thermoplastic elastomer. The mechanical properties at large deformation were analyzed at different temperatures. The copolymer shows good elastic properties, in terms of deformation reversibility as well as of energy dissipation in the hysteresis cycles. Also the stress level and the elastic recovery are very good, if compared with others thermoplastic elastomers. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In recent years the use of organometallic compounds as polymerization catalysts has allowed a very rapid development of block copolymers with a wide range of structures and related properties.[1-6] Among them, thermoplastic elastomers are raising up a great interest both from the theoretical and from the technological point of view.[7-10] The presence of long sequences of a particular monomer in a copolymer may result in incompatibility at the submicroscopic level. In these conditions, glassy or crystalline domains, behaving as physical crosslinks, can be segregated in an amorphous matrix. The elastic behavior is lost at the glass transition temperature or at the crystalline melting temperature, above which the copolymer can be processed as a thermoplastic material. Therefore a system based on the physical crosslinking can behave as an elastomer within the limits of thermal stability of the hard domains.

So far the most studied systems were the butadiene and styrene, as well as the isoprene and styrene block copolymers.[11-15] They are strong rubbers capable of large, and reversible deformation, in which the physical hard phase is constituted by the polystyrene blocks, having the glass transition well above room temperature. Although these systems are of special interest, due to the well-defined chain structures that can be obtained and analyzed, the efforts to synthesize and study new thermoplastic elastomers are greatly increasing in the last decade. The aim of these efforts is to obtain materials more stable to the oxidation, and to widen their thermal range of applicability. Furthermore, there is great theoretical interest in studying the origin of the elastomeric properties and the structure–properties relationships due to different chain microstructures.

Properties typical of thermoplastic elastomers can be obtained also in homopolymers in which a random distribution of steric errors reduces the crystallinity, inducing an elastic behavior; recently a new class of polymers having this structural feature has been prepared using propene as monomer.[16-18]

The use of homogeneous catalysts provided the possibility of copolymerizing ethylene and styrene, obtaining a series of copolymers, varying in composition and monomer distribution, as reported in a previous paper.[19] The insertion of styrene units

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Journal of Applied Polymer Science, Vol. 58, 1701–1706 (1995)
CCC 0021-8995/95/101701-06

into the polyethylene chains interrupts the possibility of long sequences in the crystalline domains, creating mainly amorphous systems, in which short chain segments can segregate into small crystalline domains, acting as physical crosslinks.

In this paper we analyze the structural organization and the related mechanical behavior of a random styrene–ethylene copolymer, showing thermoelastic behavior. The purpose of this study is to find a correlation between composition and distribution of the monomers into the polymer, chain microstructure, structural organization, and physical behavior in the series of ethylene–styrene copolymers.

MATERIALS

A Buchi glass autoclave, previously evacuated and thermostated at 50°C, was filled with 100 mL of a solution of anhydrous toluene containing 2.0 mmol of methylalumoxane and 0.02 mmol of cyclopentadienyl titanium trichloride ($CpTiCl_3$).

Then sequentially 50 mL of anhydrous styrene and ethylene at a pressure of 6 atm was introduced. The reactor was kept under stirring at constant temperature and pressure of gaseous monomer for 90 min. Then the ethylene was vented off and the mixture was discharged in 300 mL of methanol acidified with HCl. The copolymer was recovered by filtration, washed with fresh methanol, and dried *in vacuo*. The yield was 3.5 g.

The copolymer was pressure molded, in a Carver hot press, into a film shape 0.01 cm thick, and rapidly quenched in an ice-water bath (sample A). Sample A was annealed at 70°C (sample B).

EXPERIMENTAL

NMR spectrum was recorded on an AM Bruker operating at 62.89 MHz in the Fourier transform mode at a temperature of 413 K. A sample of 50 mg of copolymer was dissolved in 0.5 mL of a mixture of tetrachloro-1,2-dideuterioethane and trichlorobenzene (1 : 1 vol ratio) into a tube (5 mm outer diameter). Hexamethyldisiloxane was used as internal reference.

Infrared spectra were detected at room temperature by using a Nicolet 5DXB FTIR spectrophotometer, collecting 30 scans. The resolution was 4 cm^{-1}.

Wide-angle X-ray diffractograms were obtained by using a PW 1050 Philips powder diffractometer (CuK_α–Ni filtered radiation). The scan rate was $2°\vartheta$/min.

The thermal analysis was carried out over the temperature range −70 to 150°C using a Mettler TA 3000 DSC, purged with nitrogen and chilled with liquid nitrogen. Runs were conducted on samples of about 10 mg at a heating rate of 20°/min.

The dynamic–mechanical analysis was carried out in axial stretching, with an excitation frequency of 110 Hz, using a Rheovibron viscoelastometer (Toyo Instruments). The dynamic spectrum was detected in the range −100 to 120°C.

The stress–strain behavior was analyzed at different temperatures using an Istron 4301 dynamometer, equipped with an Istron temperature chamber 3119. The clamps displacement rate was 10 mm/min, and the initial length of the sample was 10 mm.

RESULTS AND DISCUSSION

Chain Microstructural Analysis

The composition of the E–S copolymer was determined by ^{13}C-NMR analysis.

Only five signals in the aliphatic region of the NMR spectrum have been detected at δ 23.5, 25.7, 27.8, 35.0, and 44.3 ppm from HMDS. Such a pattern of signals can be related to the presence of the triads EEE, EES + SEE, ESE, and SES.[19] No signals referable to the presence of SS sequences were detected. The ratio ethylene units/styrene units in the copolymer has been determined from the areas of the peaks using the following relationship:

$$\frac{[E]}{[S]} = \frac{\frac{1}{2}(A_{23.5} + A_{25.9} + A_{28.4} + 0.5A_{35.0})}{\frac{1}{2}A_{35.0}}$$

The value of this ratio is 4.0, corresponding to a styrene units content in the copolymer of 20%; the weight fraction is 52% in ethylene.

Infrared Analysis

In Figure 1(A) we report the infrared spectrum of sample A in the absorbance range 400–1200 cm^{-1}, whereas for comparison the same is reported in (B) for 5-phenylnonane (5PN), and in (C) for low-density polyethylene (LDPE). Locally the structural organization of our copolymer ought to be very similar to that of 5PN, having a phenyl group inserted into a sequence of CH_2 units; in fact the infrared spectra of sample A and 5PN, in the reported range,

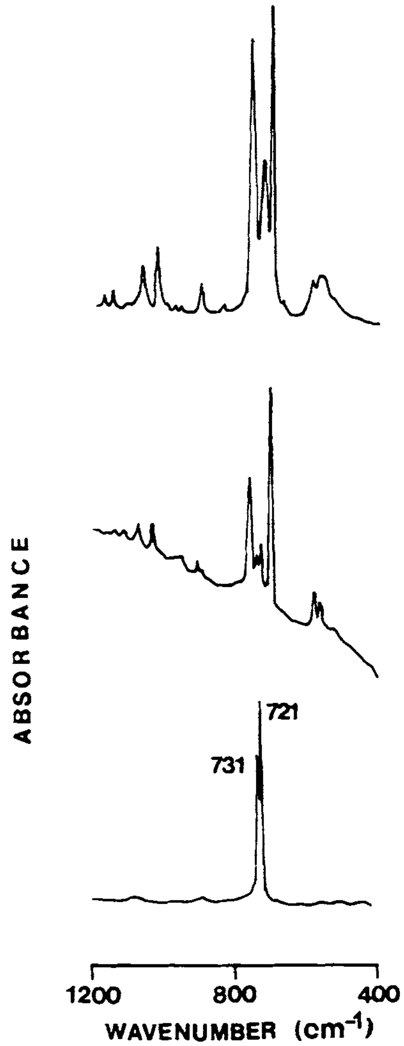

Figure 1 The infrared spectra, in absorbance (1200–400 cm^{-1}), are shown for sample A (A), 5-phenylnonane (B), and low-density polyethylene (C).

are very similar, showing the main peaks at about the same frequencies. Further information can be gained by comparing the spectrum of sample A with that of LDPE. As matter of fact, the infrared spectrum of LDPE, in the reported range, is very simple, consisting of only two bands at 721 and 731 cm^{-1}. The band at 721 cm^{-1} contains components due to both the crystalline and the amorphous phase, whereas in amorphous polyethylene it appears as a single band. The splitting into the 731 cm^{-1} band arises from the crystalline phase, and is assigned to in-phase CH_2 rocking modes for the two chains in the unit cell.[20] In sample A the peak at 731 cm^{-1} is hardly evident, and it appears only as a shoulder of the peak at 721 cm^{-1}. It is a little more evident in the annealed sample B, not reported in the figure. This is a strong indication of a low crystallinity of the polyethylene chains, whose length, limited by the insertion of the phenyl group, is not sufficient to allow a good crystallization.

Wide-Angle X-Ray Diffractograms (WAXD)

In Figure 2 we report the wide-angle X-ray diffractograms of sample A (A) and sample B (B). Both the patterns are indicative of largely amorphous samples, with two discrete peaks at 21.3 and 23.5 of 2ϑ, characteristic of polyethylene crystallinity. In particular the peak at $2\vartheta = 23.5$ appears as a shoulder in sample A, and it is more pronounced in the annealed sample B, whereas the peak at $2\vartheta = 21.3$ is well developed, and increases in intensity and in sharpness going from sample A to sample B. From the diffractograms, an approximated value of the crystallinity was calculated by comparing the area of the crystalline peaks (subtracting the amorphous contribution) with the total area. The value of crystallinity resulted 5% for sample A and 7.5% for sample B.

Differential Scanning Calorimetry (DSC)

The DSC curves, detected on sample A (A) and sample B (B), are reported in Figure 3. Sample A shows a very broad melting range, extending between 50 and 130°C, with a peak centered at 120°C, characteristic of low-density polyethylene. The wide melting range corresponds to a broad distribution of crystallite sizes, determined by the rapid cooling of the sample. The length of the ethylene units and

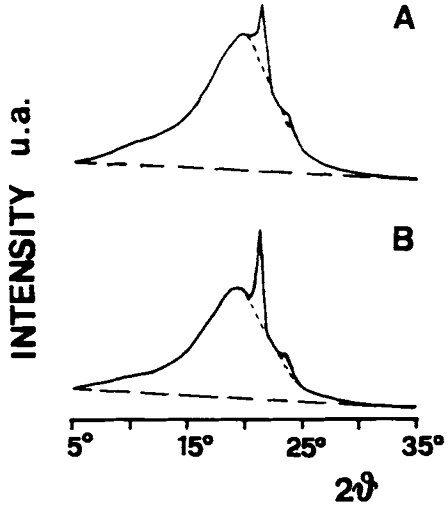

Figure 2 Wide-angle X-ray diffractograms of sample A (A) and sample B (B).

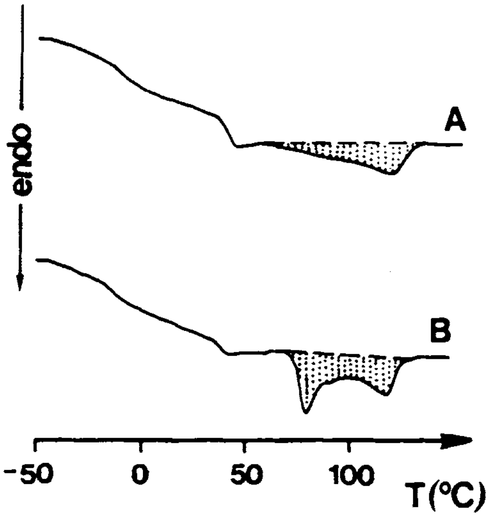

Figure 3 DSC scans of sample A (A) and sample B (B).

their distribution may limit the number of crystallites of a given thickness that can form. The annealing of this sample does not change the position of the peak at 120°C, producing instead an improvement of the more imperfect crystals. In fact a new sharp peak at 80°C, even more intense than the peak at 120°C, appears in the curve. The crystallinity results, obtained by dividing the melting enthalpy by the thermodynamic value for low-density polyethylene, i.e., 240 J/g, are very low, being 4.5% for sample A and 7.5% for sample B, well in agreement with the x-rays values.

Dynamic-Mechanical Analysis

The elastic modulus E' and the loss factor tan δ are reported in Figure 4 as a function of the temperature for sample A. The modulus shows a little variation between -100 and -15°C, going from 0.8 to 0.6 GPa; by increasing the temperature, a drastic decrease of modulus, induced by the glass transition, can be observed. From the drop of the modulus, the temperature of the glass transition can be located at 15°C. In the range from about 15 to 115°C sample A shows a definite rubbery behavior, consistent with the presence of a network structure with strong cross-links. The same trend is shown by the loss factor tan δ, which increases very rapidly at -20°C, reaching the maximum of the peak at 15°C, and then decreasing. It is worth noting that the copolymer is characterized by one glass transition, in agreement with the other structural evidences. In fact, random copolymers usually have a single T_g, between those of the corresponding homopolymers. The dependence of the T_g of a random copolymer upon composition can be predicted, assuming that there is a characteristic amount of free volume associated with each type of repeat unit, and it is the same in a copolymer or homopolymer. As is well known, theoretical calculations have led to a relationship of the form

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

where T_g is the copolymer glass transition and T_{g1} and T_{g2} are the glass transitions of the two com-

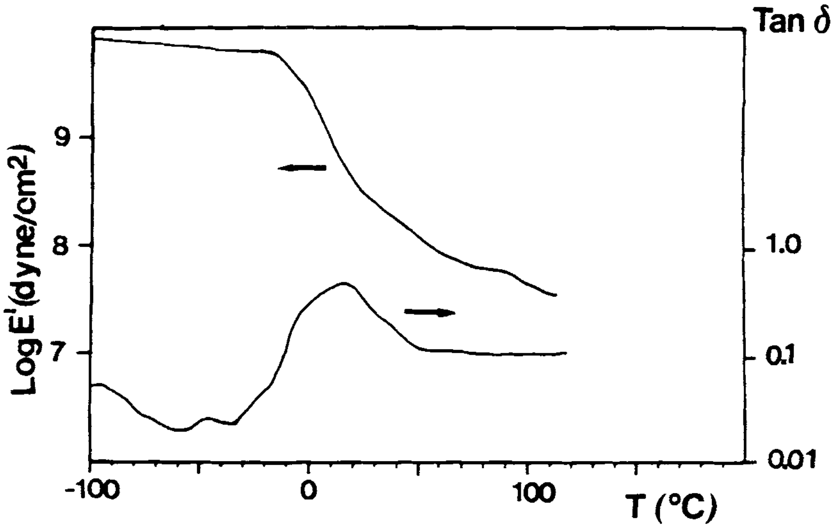

Figure 4 The logarithm of the elastic modulus log E' (dyn/cm^2), and the loss factor tan δ, are shown for sample A.

ponents, having a weight fraction, respectively, of W_1 and W_2. In our case, using for polyethylene a T_g value of 243 K, and for polystyrene a value of 368 K,[21] and as weight fractions those obtained by NMR analysis, that is 0.52 in ethylene, we obtain a T_g of the copolymer of 290 K, which is in very good agreement with the experimental value.

Elastic Behavior

The stress–strain behavior at large deformations was analyzed at three different temperatures (25, 50, and 80°C). The analysis was carried out adopting the Mullins' cycles[22]; in particular the sample was deformed at strain values progressively increasing step by step, the step being characterized by an additional deformation constant in all the cycles. The upper limit of each cycle was reached at a constant rate of the clamps displacement and then the sample was rapidly relaxed to the initial length. After 5 min of rest, the next step, characterized by a higher strain limit, was carried out. This technique is particularly useful to test the elastic behavior, to verify the reversibility of the axial deformation, and to correlate this information to the organization of the physical network. The obtained results are shown in Figure 5(A), 5(B), and 5(C), each regarding a different temperature; the stress in MPa was calculated as the force over the undeformed cross-sectional area, while the strain, indicated as lambda, was calculated as the ratio of the actual over the initial length. It is evident that stress softening follows each cycle, while, when the upper limit of the previous cycle is reached, the stress–strain curve joins the previous one. This trend determines a perfect superposition of the upper part of each curve to form a continuous stress–strain plot. Figure 5 shows also the permanent set, that is, the residual deformation after each cycle; at 25°C the reversibility of the axial deformation is typical of a good elastic behavior: in fact after the last step corresponding to $\lambda = 5$, the permanent set is only 2.2. At 50°C the elasticity is improved and, in fact, after the last step up to $\lambda = 6.3$, the permanent set is only 2.5. At 80°C the stress level collapses to very low values, indicating that the deformation is mainly due to plastic flow, even if the elasticity of the system is not completely lost. In Table I we report the elastomeric properties of sample A at 25°C. The values indicate very strong mechanical properties, and very good elastic recovery.

The trend of the elastic behavior, showing a maximum in the elastic recovery at 50°C, can be explained on the basis of two main transitions of the system, i.e., glass transition and melting. At 25°C (Fig. 5A) the system is about 10° above the glass transition, while at 80°C, the thermogram indicates the presence of the melting regime, which induces the plastic flow. Moreover another relevant aspect can be deduced from the stress–strain behavior. In fact, Figure 5 shows an evident Mullins effect, which is typical of systems characterized by unstable crosslinks which can be removed by the progressive increase of the deformation; the stress softening following each cycle is indeed the effect of a progressive decrease of the crosslinking concentration. This effect is widely observed in crosslinked elastomers, filled with carbon black, where a physical crosslinking is present due to the adesion between rubbery matrix and filler.[23] In the present case the physical crosslinking is due to the crystalline domains, where

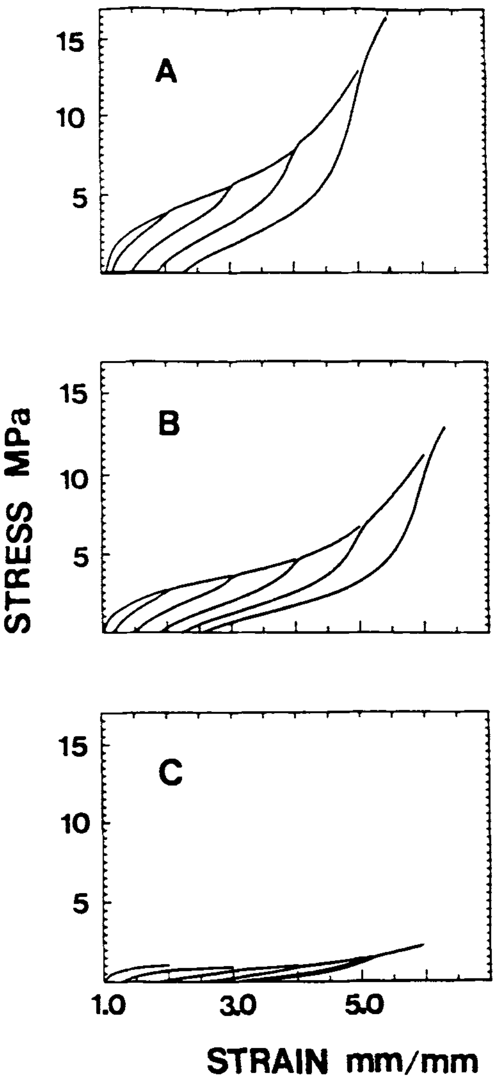

Figure 5 Mullin's hysteresis cycles for sample A at 25°C (A), 50°C (B), and 80°C (C).

Table I The Stress (MPa) and the Elastic Recovery of Sample A, at Different Strain Ratios, λ, for the Drawing at 25°C

Draw Ratio	Stress (MPa)	Recovery (%)
2	5.6	90
3	8.0	71
4	13.4	62
5	15.0	62

the instability is due to the possibility that the deformation, and therefore the stress at the molecular level, can pull chain segments out of the crystals. This effect is dramatically ruled by the temperature, and, in fact, at 80°C, that is, within the melting range (see Fig. 3), the stress collapses to very low values because the tension required to pull chain segments out of crystals in the melting regime is extremely low.

CONCLUSIONS

The most important feature of the analyzed copolymers is their elastic behavior. In sharp contrast to highly crystalline polyethylene, the copolymers styrene-ethylene show typical properties of a thermoplastic elastomer in stress-strain measurements. In fact, they show no plastic yield and have good elastic recovery. The key component responsible for the elasticity is the insertion of isolated styrene units into the polyethylene chains. This interrupts the possibility for a long segment to crystallize, and few crystalline units segregate into a prevalently amorphous matrix. Although in the quenched sample we observe a broad range of crystallite dimensions, the annealing procedure shows a dependence of the size and order of the crystalline domains on the crystallization conditions, with the tendency to reduce the melting range toward higher temperatures. This can enlarge the thermal range of applicability of this class of copolymers, since the melting temperature of polyethylene is at the high extremity of the range. Also the stress level and the elastic recovery are very good if compared with other known thermoplastic elastomers.

This work was supported by "Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate" CNR—Italy.

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Received November 29, 1994
Accepted February 9, 1995