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Effect of Casting Solvents on the Properties of Styrene–Butadiene–Styrene Block Copolymers Studied by Positron Annihilation Techniques

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ABSTRACT: The positron annihilation technique was used to study the properties of styrene–butadiene–styrene block copolymers obtained by casting them in four different solvents: toluene, carbon tetrachloride, ethyl acetate, and methyl ethyl ketone. The positron annihilation rates plotted as a function of temperature show in all films irregularities at -70 and +85 °C which were attributed to the onset of motions in the polybutadiene and polystyrene domaines, respectively. In addition to that, two irregularities were observed at -14 and +10 °C if a poor solvent, such as ethyl acetate or methyl ethyl ketone, was used, while films cast in a good solvent such as toluene or carbon tetrachloride show only one additional irregularity on the $\lambda_2 - T$ curves at -14 °C. The latter results were explained in terms of the "interfacial model" by assuming that these irregularities correspond to the glass transition of "interlayer phases" between the pure polystyrene and the pure polybutadiene phases. The one which shows the irregularity at -14 °C could be the phase in which polybutadiene is the major component, while the transition at +10 °C can be attributed to a phase in which polystyrene is the dominating factor.

Recent reports on the styrene–butadiene–styrene system (SBS) block copolymer types[1-5] have shown that the morphology, and concomitantly the final properties of these systems, can be influenced by the nature of the conditions used in preparing the polymer films. The effect of the casting solvent on the bulk properties on the linear S–B–S block copolymer has been reported in the literature.[2,3] Because of differing and controversial experimental results in these previous studies, it appeared worthwhile to reinvestigate this polymer by using a novel technique, the positron annihilation method, to determine the effect of the solvent used to produce the film on its final properties.

The positron annihilation technique[6] has been employed successfully as a method for investigating phase transitions and structural changes in molecular crystals,[7] liquid crystals,[8-11] and, more recently, micellar[12-19] and biological systems.[20] Although it has been demonstrated that the intensity and the lifetime of thermal orthopositronium depend on the physical and chemical properties of the polymer,[21-25] the application of this method for studying polymer systems has been very limited. It was found that these parameters vary as a result of the changes which may occur in the chain structure, configuration, conformation, and molecular weight distributions of the samples.

The results of these previous studies demonstrate clearly the applicability of the technique for these systems. Moreover, recent significant results obtained in our laboratory on complex systems such as micelles[12-19] and liposomes[20] have led us to the conclusion that this technique has not been fully exploited in polymer systems. Thus, in the following the positron annihilation technique was utilized to investigate the properties of S–B–S block copolymers obtained by casting in four different solvents: toluene, carbon tetrachloride, ethyl acetate and methyl ethyl ketone.

Experimental Section

A. Purity of Material and Film Preparation. The S–B–S block copolymer used in these studies was Solprene 416 (sample No. 52169). It was obtained from Phillips Petroleum Co. The nominal styrene content in the copolymer is 30%. The inherent viscosity is 1.91 in THF at 25 °C, the average number molecular weight is 124000, and the weight average molecular weight is approximately 140000. The solubility parameters of the styrene block and butadiene block were reported in the literature and assumed to be 9.4 and 8.6, respectively.[2] The solubility parameters (δ) of the solvents used in these studies are[26] for toluene 8.9, for carbon tetrachloride 8.6, for ethyl acetate 9.1, and for methyl ethyl ketone 9.3.

The polystyrene used had a molecular weight corresponding to the nominal styrene content in the copolymer. It was molded at 150 °C.

The samples were prepared for the measurements from solution by casting them on glass plates and removing the solvent under vacuum at 80 °C. The solvents, such as toluene, carbon tetrachloride, ethyl acetate, and methyl ethyl ketone, were obtained from Fisher Scientific Co. and used without further purification.

B. Positron Lifetime Measurements and Preparation of the Samples. Positron lifetime measurements were carried out by the usual delayed coincidence method as previously described.[27] The resolution of the system, as measured by the fwhm of the prompt coincidence spectrum of a ^{60}Co, without changing the 1.27 and 0.511 MeV bias, was found to be less than 0.34 ns fwhm. The positron source consisted of 3–5 μCi ^{22}Na evaporated onto a thin foil of aluminum. The ^{22}Na source was sandwiched between two stacks of polymer disks with a total thickness of each stack of about 2.5 mm, which is sufficient to assure that all positrons annihilate in the polymer. The sample was transferred into a specially designed cylindrical vial and then carefully degassed. The vials were subsequently sealed under vacuum, and the measurements were carried out at various temperatures in a specially designed cryostat which allowed us to control the temperature to within ±0.5 °C. At least two lifetime measurements were performed at each temperature. The experimental error in the λ_2 values is approximately ±2%.

C. General Method of Data Analysis. The positron annihilation parameters were obtained by standard computational techniques. The lifetime spectra were resolved as previously described[28] into two components, a short-lived component, which is the result of p-Ps annihilation, free positron annihilation and epithermal Ps interactions, and the long-lived component, with a decay constant λ_2 and its associated intensity I_2, which is generated by the reactions and subsequent annihilation of thermalized o-Ps. The lifetime data analysis was performed by applying the PAL program.[29]

Results and Discussion

In the first series of experiments, positron annihilation parameters were measured as a function of temperature in S–B–S block copolymers which were cast in different solvents, such as toluene, carbon tetrachloride, ethyl acetate, and methyl ethyl ketone. As Figure 1 shows, λ_2, the annihilation rate of the thermalized o-Ps atoms, changes as a function of temperature in all systems under study.

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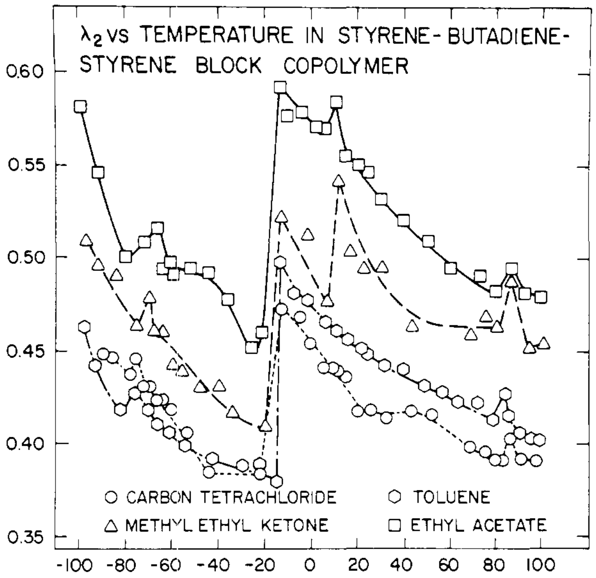

Figure 1. Plot of λ_2 vs. temperature in styrene–butadiene–styrene block copolymers cast in toluene, carbon tetrachloride, ethyl acetate, and methyl ethyl ketone. Typical experimental error $\pm 0.01 \times 10^9$ s.

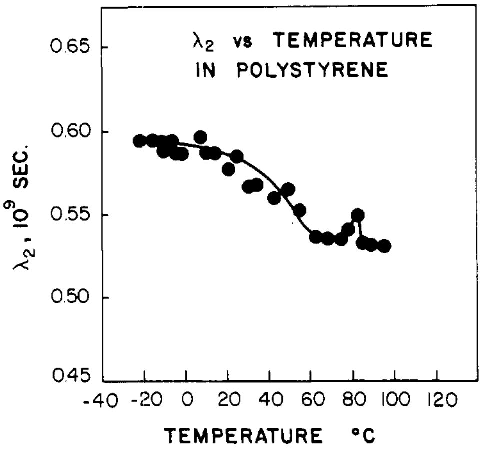

Figure 2. Plot of λ_2 vs. temperature in polystyrene (molded at 150 °C). Typical experimental error $\pm 0.01 \times 10^9$ s.

In all films, an abrupt increase of I_2 followed by a subsequent decrease over a relatively small temperature range is observed at −70, −14, and +85 °C.[30] An additional well-defined abrupt change in λ_2 at +10 °C appears in the $\lambda_2 - T$ plots of films from "poor" solvents (ethyl acetate and methyl ethyl ketone).

In the second series of λ_2 the positron annihilation parameters were determined in pure polystyrene which had been molded at 150 °C and which had a molecular weight equal to the nominal styrene content in the S–B–S copolymer, as a function of temperature.

As Figure 2 shows, where λ_2 is plotted as a function of temperature, the positron annihilation rate decreases rather smoothly over the measured range −20 to +80 °C and displays only one abrupt change at +85 °C. This temperature corresponds to the glass transition temperature of this polymer, and the peak in the λ_2 – temperature plots of the S–B–S copolymers has therefore been related to the onset of motion in polystyrene. In analogy, the change at −70 °C in the same plots has been attributed to the glass transition of polybutadiene.

While these observations, i.e., the changes at −70 and +85 °C, are in general agreement with previous results reported in the literature,[2,3] some disagreement seems to exist about the existence and origin of the intermediate peaks at −14 and +10 °C.

Miyamoto et al.[3] reported the existence of a third peak in their mechanical loss curves and DSC thermograms in the case of polymer films cast from poor solvents (ethyl acetate and methyl ethyl ketone) in their studies with the Rheo-Vibron technique and differential scanning calorimetry. The first technique demonstrated the existence of a third peak at +10 °C; whereas if the second method was applied, a peak was observed at −14 °C. Miyamoto et al.[3] interpreted these peaks at +10 and −14 °C observed via the Rheo-Vibron technique and differential calorimetry, respectively, as originating from the same phenomenon, the temperature shift probably due to the different sensitivity of the techniques used.

Similar studies had been performed by Beecher et al.[5] on styrene–isopropene–styrene, using a vibrating reed apparatus. These authors reported the presence of a broad intermediate transition (−26 to 4 °C) between the pure polystyrene and polyisoprene.

On the other hand, Rheo–Vibron studies on the S–B–S block copolymers by Wilkes et al.[2] did not reveal the presence of any transitions in the intermediate temperature range, i.e., between −50 and +50 °C.

In the present studies, we could clearly identify the presence of two intermediate changes in the annihilation rate λ_2. The one which was observed in poor solvents at +10 °C supports the Miyamoto Rheo–Vibron results,[3] while the second change in λ_2 observed in all S–B–S block copolymers at −14 °C could correspond to that detected by the differential scanning calorimetry technique.[3]

Changes of λ_2 in molecular substances, polymers, etc., have been interpreted by Brandt et al.[7,31,32] in terms of "free volume" theory. According to Brandt, the temperature and phase dependence of the annihilation rate of o-Ps (λ_2) in molecular substances is primarily a "free volume" effect in that the overlap between the positron component of the o-Ps wave function and the wave function of the lattice electron involved in Ps formation depends on the lattice space. In other words, as the size of the individual cavities in the polymer increases with temperature, the annihilation rate of the thermal orthopositronium decreases.

The observed changes of λ_2 at the glass transition temperature may then be interpreted as follows.[23b] The onset of molecular motion first causes the diffusion of electron density into the free volume, which is occupied by the o-Ps. Therefore, a slower reduction or even an increase of the annihilation rate can be expected. As the temperature further increases, a point may be reached at which the Ps pressure exerted on its environment may cause a sudden increase in the free volume if the surrounding chain segments become flexible enough. This leads to a distinct decrease in the annihilation rate. Above this temperature, a further smooth correlation between λ_2 and temperature will exist.

As already discussed above, the irregular changes observed in the λ_2-temperature plots of S–B–S block copolymers at −70 and +85 °C can be identified as the onset of motion in the polybutadiene and polystyrene domaines.

To explain the irregularities at intermediate temperatures, one could invoke the suggestions by Miyamoto et al.[3] and Beecher et al.,[5] who assumed that the boundary between the polystyrene and polybutadiene (or polyisopropene) domaines is not a sharp one and therefore the degree of separation between them is imperfect.[33] As a result, the pure polystyrene and polybutadiene (or polyisoprene) domaines are expected to be separated by an intermediate layer in which both polystyrene and polybutadiene are present in molecular mixtures.

The existence of such an interlayer has been postulated by Kaelbe[34] in the so-called "interfacial model" or "adsorption–interdiffusion model". This model postulates the existence of an interfacial SB (or SI) phase which separates the S and B phases. This interfacial phase can be regarded as a third component in the S–B–S copolymer.

The experimental results obtained by Miyamoto[3] (Beecher[5] on S–I–S) and by the present positron annihilation studies seem already to indicate the existence of a more complicated interlayer phase. Miyamoto,[3] as well as Beecher,[5] reported the presence of a broad third peak (−30 to +50 °C) in his studies with the Rheo–Vibron technique. According to these authors,[3] the same change is detected at −14 °C by DSC. This difference has been previously explained in terms of a poor resolution of both techniques. On the other hand, the positron annihilation technique clearly demonstrated the existence of two irregularities in λ_2 vs. T at intermediate temperatures.

Thus, according to the "interfacial model",[34] it seems reasonable to attribute these changes to the glass transition of the interlayer phase between the pure polystyrene and the pure polybutadiene phases. The one detected at −14 °C, in all films, is assumed to correspond to a phase in which the major component is polybutadiene, while the second, which is observed at +10 °C in poor solvents, is attributed to a phase where the polystyrene is the major component.

In conclusion, we feel that the data reported here provide new insights into the properties of polymeric systems and also demonstrate the future potential of the positron annihilation technique in this area.

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(30) The intensity I_2 associated with the long-lived component in the positron lifetime spectra shows also a temperature dependence. However, since I_2 depends on the magnitude of λ_2 in a rather involved manner (for a discussion of these aspects see, e.g., H. J. Ache, R. E. Wild, and L. F. Bartal, *J. Phys. Chem.*, 81, 941 (1977)), no attempt has been made to correlate I_2 with the polymer properties. Correlations of I_2 with structural changes, etc., are usually only valid if λ_2 is not significantly affected by these changes. It should also be pointed out that it is difficult to reproduce the absolute values of λ_2 in samples cast from different solvents or from one simple to the other, while the trends, irregularities, etc., are easily reproducible.

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