Blends of head-to-head polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide)*

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Blends of head-to-head polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) were prepared and found to be miscible as judged by a single T_g The measurements were carried out by d.s.c and dilatometry. At high concentrations of PPO ($>80\%$) the mixture is on the threshold of incompatibility as indicated by the increase of the width of the transition step increase by d.s.c. and the increase of the free volume as calculated from dilatometric data. The thermal stability studies of head-to-head polystyrene-(HH-PS)-poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends by thermal volatilization analysis show two decomposition processes in the temperature range characteristic for both homopolymers The temperature of the maximum rate of decomposition for PPO in the blend is slightly shifted towards lower temperatures as compared with pure PPO. This can be explained by assuming that the PPO degradation is induced by radicals formed during the decomposition of HH-PS.

Keywords Characterization; measurements; calorimetry; dilatometry; thermal stability, polystyrene

INTRODUCTION

Blends of atactic head-to-tail polystyrene (HT-PS) with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been found to show complete miscibility over the whole range of compositions and have been successfully commercialized under the trade name of Noryl[1-5]. This was the first example of miscible polymers where the individual component polymers have substantially different polymer structure. Since this work was done, it was found that other styrene polymers have only limited miscibility with PPO, and many are even nonmiscible[6-9]. Of particular interest were the miscibility studies of polymers of *o*-chlorostyrene and *p*-chlorostyrene and their copolymers with styrene[6-8] with PPO.

Head-to-head polystyrene (HH-PS) has been synthesized and its structure and sterochemistry were characterized by chemical and spectroscopic means[10,14,15], solution properties[11], dielectric properties[12], and degradation characteristics[13] were also studied, and HH-PS and HT-PS were investigated for their comparative melt rheological behaviours[16].

The value of the T_g of HH polymers has become of interest as the T_g represents a measure of the flexibility of the polymer chain. It has been shown that polymers of polar monomers have higher T_g's when the monomers are arranged in an HH fashion[17]. Such an example would include the HH polyacrylates which show T_g's 30–40°C higher than the corresponding HT polymers. However, nonpolar HH polyolefins had lower T_g's than the corresponding HT polymers. Most surprising was the fact that atactic HT-PS obtained by radical polymerization and HH-PS showed nearly the same T_g with the T_g of the isotactic HT-PS only 5–6°C lower[10]. This effect was explained by a fortuitous balance of steric and electronic factors influencing the solid state properties of PS which are responsible for the value of the T_g[18,19].

It was consequently of interest to study and compare blends of HH or HT polymers with other polymers, particularly blends of PS with PPO. These blends were studied by d.s.c. and dilatometry over the whole range of composition; their degradation behaviour was also investigated.

EXPERIMENTAL

Materials

Head-to-head polystyrene (HH-PS) was prepared from 1,4-poly(2,3-diphenylbutadiene) by chemical reduction with potassium/ethanol in THF. The 1,4-poly(2,3-diphenylbutadiene) was obtained by free radical polymerization in bulk at 60°C with AIBN as the initiator. The polymers consisted of only 1,4 linkages at a *cis–trans* ratio of nearly 1:1. The chemical reduction of 1,4-poly(2,3-diphenylbutadiene) seems to be stereospecific and gave HH-PS with nearly a 1:1 ratio of erythro and threo linkages[10]. The reduction had to be performed twice to complete the reaction[10]. HH-PS had a M_w/M_n of about 2 and a M_n of about 40 000 according to g.p.c. Additional characterization of this HH-PS was described earlier[11].

Head-to-tail atactic polystyrene (HT-PS) of approximately the same M_n and the same molecular weight distribution as the HH-PS was prepared by bulk polymerization of styrene with AIBN.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of [$\bar{M}_n = 17\,000$, $\bar{M}_w = 36\,200$, $M_w/M_n = 2.07$] was obtained from the General Electric Company. The polymer mixtures were prepared by dissolving HH-PS and PPO in toluene (3-4%) and coprecipitating into methanol. The precipitate was washed twice with methanol and then dried overnight at 0.1 mm Hg at 60°C.

Measurements

A Perkin-Elmer DSC II was used to study the glass transition of the blends and the blend components. The

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* Communication XIV on head-to-head polymers

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temperature scale of the instrument was calibrated at the desired heating rate by adjusting the direct dial average temperature readout of the programmer to correspond with the transition temperature of indium (m.p. 429.78K) and tin (m.p. 505.06K). The d.s.c. samples were prepared by pressing the dried, precipitated blends into aluminium d.s.c. pans which were then sealed. The weight of each sample, typically 16–18 mg, was measured by a Perkin–Elmer AD-2 Autobalance to a precision of 0.01 mg. A heating rate of 20K $\min^{-1}$ and a range of 2 mcal s^{-1} was used for each sample while chart settings (Perkin–Elmer model 56 recorder) were 10 mV at a speed of 20 mm $\min^{-1}$. Samples were heated from 275K to 525K under a nitrogen purge of 15 psi, then were immediately cooled at 80K $\min^{-1}$ back to 275K. The samples were then programmed back to 525K at the heating rate described. These thermograms were used to calculate the glass transition temperatures (T_g's) by finding the mid-point of the transition in the normal way (second heating).

Thermal expansion coefficients as well as glass transition temperatures for the homopolymers and blends were determined by the use of dilatometric method in the temperature range 50°–250°C at a cooling rate of 5°C $\min^{-1}$. A Bekkedahl type dilatometer, which was filled under vacuum with mercury, was used[20].

Thermal expansion coefficients α_L, α_g and $\Delta\alpha=\alpha_L-\alpha_g$ were found from the slopes of the straight lines $V_s=f/T$. The estimated error of calculation of the α_L and α_g values equals about 10%. The subscripts L and g refer to the liquid and glassy states of the polymer respectively. V is the specific volume, f is a constant and T is the temperature.

T_g's found from the intersection points of two straight lines are dependent on the difference of the slopes $\Delta\alpha$. It was estimated that in the most unfavourable case the error of T_g determination was about 2%.

The error of T_g determination using d.s.c. measurements is ±2°C, thus the experimental precision is high enough to detect any deviation from the Gordon–Taylor equations[21].

Thermal volatilization analysis (t.v.a.) was carried out using a single line condensation system[22]; the temperature of the first trap was 25°C and the main trap −196°C. The weight of the sample was typically 20–50 mg. Degradation products were analysed by gas chromatography with a GCHF 18.7 apparatus equipped with a hydrogen flame ionization detector. Separation conditions and synthesis of appropriate model compounds are described elsewhere[23,24].

Gas chromatography–mass spectrometry (g.c.–m.s.) analysis was carried out with a 2091 LKB gas chromatograph–mass spectometer connected to a PDP 11 digital computer. The identity of the g.c. peaks was established on the basis of the mass spectra either by comparing the mass spectra of these compounds with the mass spectra of appropriate models or by analysing the fragmentation scheme. The ratios (wt. fraction of rearranged dimers)/(wt. fraction of unrearranged dimers) and (wt. fraction of dimers)/(wt. fraction of monomers) were determined by gas chromatography. The following model compounds were used as calibration: 2-Methylphenol, 2,4-dimethylphenol, 2,6-dimethylphenol, 2,4,6-trimethylphenol for monomers, 2-(3,5-dimethyl-4-hydroxybenzyl)-4,6-dimethylphenol for rearranged dimers, and 2,6-dimethyl-4-(3',5'-dimethyl-4'-hydroxyphenoxy) benzene for unrearranged dimers. The estimated error of these measurements (about 15%) indicates that the difference of the product ratios is beyond experimental variation.

Blend densities at 25°C were calculated from the sum of the products of component weight fractions and specific volumes, i.e.

$$\frac{1}{\rho}=\frac{C_1}{\rho_1}+\frac{C_2}{\rho_2}$$

where C and ρ are weight fractions and densities respectively. Density of PPO and HH-PS were taken to equal 1.06 and 1.02 g cm^{-3} respectively.

The expression for calculating the specific volume of the sample as a function of the temperature is the following[24]:

$$V_s=\frac{m_{Hg}}{m_p d_{Hg}(25°C)}(\alpha_{Hg}-\alpha_s)\Delta T+\frac{1+\alpha s\Delta T}{d_p(25°C)}+\frac{\Delta hS}{m_p} \qquad (1)$$

where ΔT, the temperature difference relative to 25°C; $\alpha^s=14.2\cdot10^{-6}$, volume thermal expansion coefficient of the glass; $\alpha_{Hg}=1.8\cdot10^{-4}$ deg^{-1}, volume thermal expansion coefficient of mercury; m_{Hg}, mass of mercury which was typically 5–6 g; $S=2.366\cdot10^{-3}$ cm^2, cross section area of the capillary; Δh, difference of the mercury column height relative to the height at 25°C; d_{Hg} (25°C) = 13.534 g cm^{-3}, density of mercury at 25°C; m_p, mass of the polymer sample, typically 30–50 mg; d_p (25°C), density of the polymer sample at 25°C.

It can be shown, by introducing the indicated values into equation (1) that possible deviation from the volume additivity can have little or practically no effect on the discussed values of T_g temperatures or thermal expansion coefficients.

Free volume is defined according to Simha and Boyer as[25]:

$$K_1=\Delta\alpha\cdot T_g$$

where K_1 is a constant approximately equal to 0.113 for a wide variety of amorphous polymers.

$$\alpha_L=(\Delta V_s/\Delta T)_T>T_g$$

$$\alpha_g=(\Delta V_s/\Delta T)_T<T_g$$

$$\Delta\alpha=\alpha_L-\alpha_g$$

RESULTS AND DISCUSSION

Compatibility of head-to-head polystyrene–poly(2,6-dimethylphenylene oxide) blends

By d.s.c. and dilatometry, the blends of HH-PS-PPO are compatible in the whole range of compositions. *Figure 1* shows the d.s.c. curves obtained for various compositions of the blend with all samples exhibiting a single glass transition temperature (T_g). The step width of the glass transition, as defined by MacKnight and Karasz[7], varies for blends of different composition. As can be seen in *Figure 2* this width was 6°C for pure HH-PS and increased slowly to 20°C for the blend of 80% of PPO and 20% HH-PS indicating a possible approach to the region of incompatibility.

Polymer blends showing single glass transitions

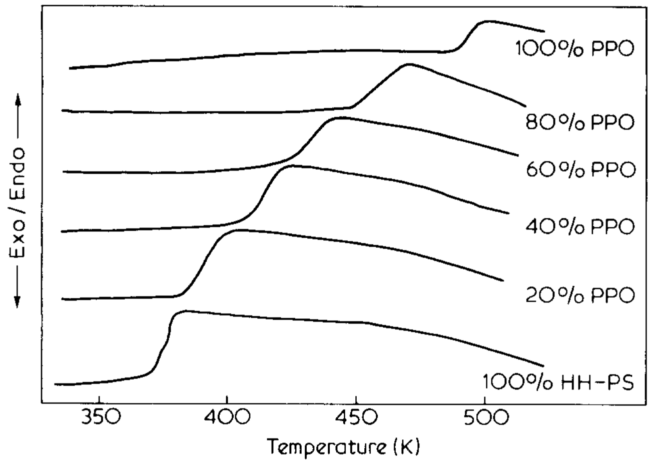


Figure 1 D.s.c. thermograms of HH-PS, PPO and the blends HH-PS—PPO of various compositions

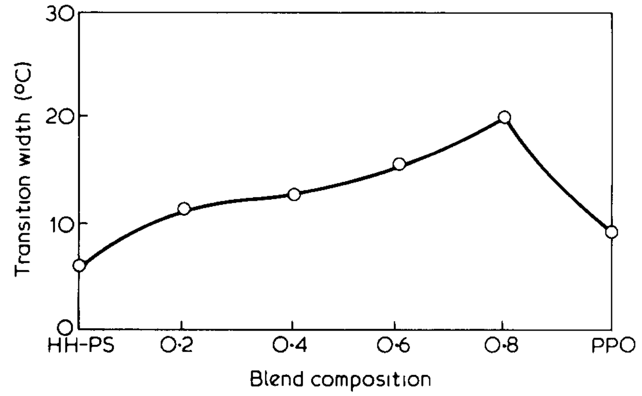


Figure 2 Width of the glass transition of the blends HH-PS—PPO as a function of blend composition

indicate that the blends are compatible. However, broadening of the glass transition as measured by d.s.c., indicates that the transition is on the threshold of the region of incompatibility where broadening was observed to be the greatest[26,27]. The broadening of the width of the glass transition in vinyl copolymers of different degrees of chemical heterogeneity and for polymer blends of different compositions[7] was explained in terms of the interactions between neighbouring chain segments. It has been suggested that if the interaction of a chain segment of the polymer chain with its nearest neighbour begins to change in degree of interaction, the temperature range over which the glass transition takes place becomes more diffuse because heterogeneous systems possess regions that are very closely spaced but also regions of low degree of interaction. This observation can be seen better by dilatometric measurements which also confirms the d.s.c. data.

Dilatometric measurements showed single T_g. Specific volume data plotted against temperature and their dependence for homopolymers and blends of various compositions is shown (*Figure 3*). From this figure the thermal expansion coefficients below and above the glass transition can be determined. The T_g values found by d.s.c. and dilatometry based on blend composition are shown in *Figure 4* and compared with the curve calculated according to the well known Gordon–Taylor equation[21]:

$$T_g = \frac{C_1 \Delta\alpha_1 T_{g1} + C_2 \Delta\alpha_2 T_{g2}}{C_1 \Delta\alpha_1 + C_2 \Delta\alpha_2}$$

where C_1, C_2 are weight fractions of HH-PS and PPO in the blend respectively; T_{g1}, T_{g2} are glass transition temperatures of HH-PS (98°C) and PPO (207°C) respectively; $\Delta\alpha_1$, difference in thermal expansion coefficients above and below T_g for HH-PS found to equal 3.75×10^{-4}; $\Delta\alpha_2$, difference in thermal expansion coefficients above and below T_g for PPO found equal to 2.6×10^{-4}.

As can be seen in *Figure 4* all the T_g values found by dilatometry are lower than the corresponding T_g values obtained from d.s.c. measurements. Such a result may be attributed to the fact that d.s.c. measurements were made by increasing the temperature with a heating rate of 20°C min^{-1} while dilatometric measurements of specific volume were carried out by decreasing the temperature with the cooling rate of 5°C min^{-1}. The Gordon–Taylor equation predicts T_g's of the polymer blends between the values observed by the two experimental techniques (*Figure 4*).

Figure 5 shows the composition dependence of thermal expansion coefficients below and above T_g temperature as well as free volume as defined by Simha and Boyer[25]. At low PPO content, the value of the free volume for the mixtures is lower than the values that one would obtain if one would expect a linear dependence. This observation suggests a relatively better packing of the HH-PS and PPO chains. At low HH-PS content, the free volume values are above the straight line which indicates linear

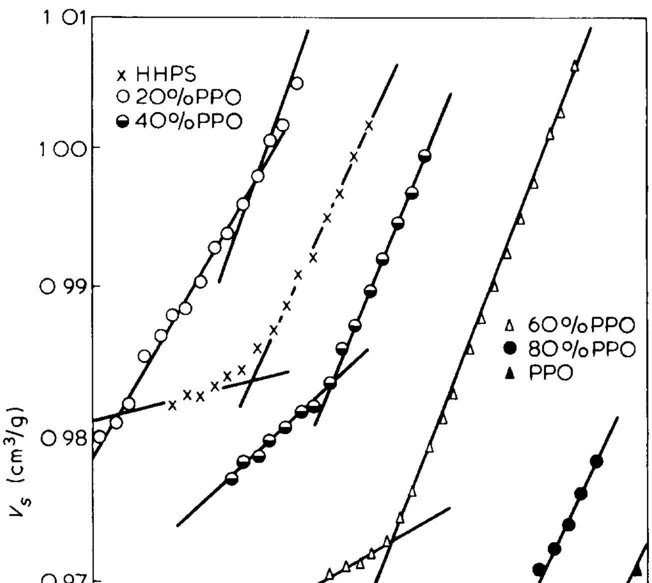


Figure 3 Plot of specific volume *versus* temperature for HH-PS, PPO and the mixtures HH-PS—PPO of various compositions

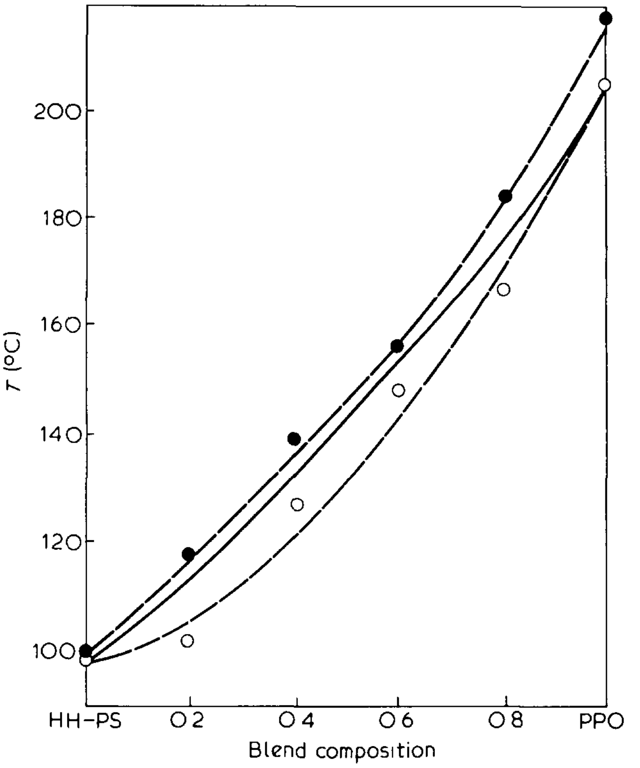


Figure 4 Glass transition temperatures of the mixtures PPO—HH-PS obtained from d.s.c. (●), dilatometry (○) and calculated according to G—T formula (—) as a function of HH-PS—PPO content in the blend

dependence. In such a case the packing of the two components of the blends is unfavourable. This result correlates well with the composition dependence on the width of the transition, showing that polymer blends with around 20% HH-PS are the least miscible blend composition.

Thermal degradation studies

It has been shown in our previous report that HT-PS interacts with PPO during thermal degradation^{28}. The use of nonisothermal techniques such as t.g.a. and t.v.a. showed that the HT-PS decomposition is slightly retarded in the presence of PPO. Detailed analysis of the degradation products as well as the process kinetics by isothermal thermogravimetry indicate that the presence of PPO interferes with the intermolecular chain transfer reaction and changes the course of the intramolecular chain transfer. In view of these results, it seemed interesting to test the thermal stability of the mixtures of HH-PS with PPO which was reported to undergo purely statistical scission on heating^{13}. *Figure 6* shows the comparison of t.v.a. traces obtained for a sample of 50% HH-PS and 50% PPO without special mixing (a), and for the carefully prepared physical mixture of HH-PS and PPO (b), which was found to be homogeneous by d.s.c. and dilatometric measurements. In *Figure 6a*, the peak with the maximum at about 380°C can be assigned to HH-PS (by comparison with the t.v.a. trace of pure HH-PS) while the peak of maximum degradation at about 440°C can be assigned to PPO. In *Figure 6b* the position of the HH-PS peak remains unchanged while the maximum rate of PPO decomposition is shifted by about 10°C towards lower temperatures. It can be concluded that the stability of HH-PS is not affected by the presence of PPO. Alternatively, the thermal decomposition of HH-PS exerts a destabilizing effect on PPO apparently because of the influence of the radicals formed during the degradation. Such an influence was not observed for HT-PS–PPO mixtures. This lack of interference during the degradation of this mixture is attributed to the low reactivity of the radical species formed during decomposition of HT-PS which are substantially resonance stabilized radicals substituted with the phenyl group. The peak at about 125°C (*Figure 6b*), is not related to the degradation behaviour of the blend HH-PS–PPO but is attributed to trace amounts of residual toluene used as solvent for the preparation of the polymer blends.

The product analysis obtained by g.c.–m.s. for the HH-PS degradation is shown in *Figure 7*. The mass spectra obtained for the individual decomposition products of HH-PS allowed the following interpretation of the HH-PS decomposition mechanism (see also ref. 13): Initial cleavage of the carbon–carbon bond either between the two phenyl substituted carbon atoms (a), or between one phenyl substituted carbon atom and the carbon atom of the adjacent methylene group (b).

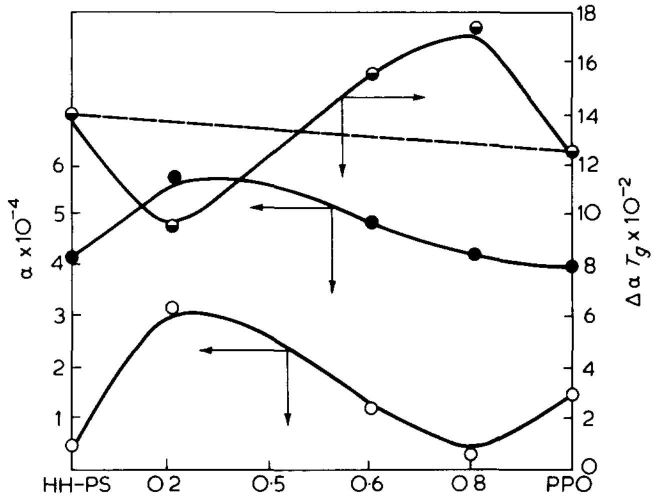


Figure 5 Composition dependence of free volume (◐) and thermal expansion coefficients below (○) and above (●) glass transition temperature

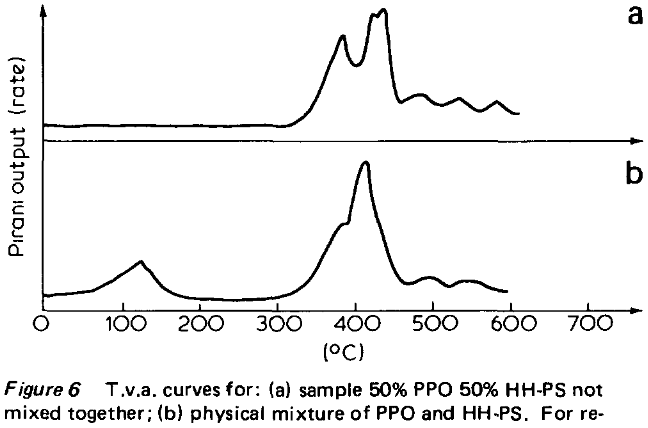


Figure 6 T.v.a. curves for: (a) sample 50% PPO 50% HH-PS not mixed together; (b) physical mixture of PPO and HH-PS. For results on both curves (t.v.a.) the condenser was at room temperature

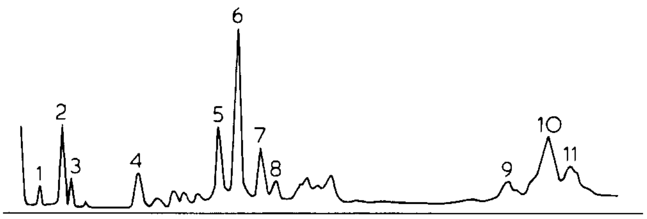
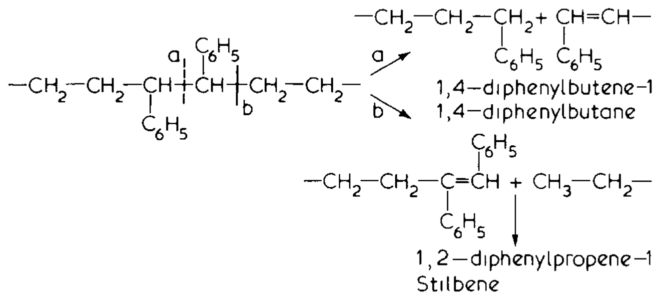
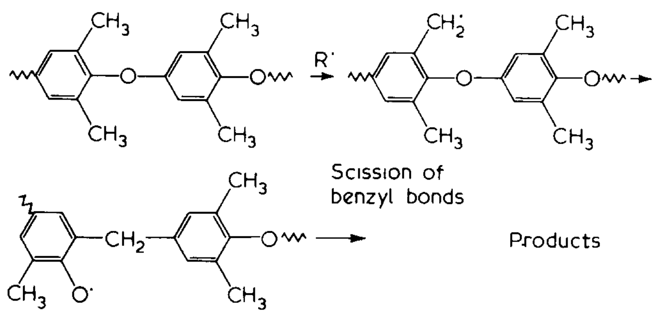


Figure 7 Gas chromatogram of HH-PS degradation products: (1) styrene; (2–3) not identified; (4) 1,2-diphenylethylene; (5) 1,2-diphenylpropene-1; (6) 1,4-diphenylbutane; (7) 1,4-diphenylbutene-1; (8) 1,4-diphenylpentane; (9) 4,5-diphenyl-1,8-octadiene; (10) 2,3,6-triphenylhexene-1; (11) 1,4,5-triphenylpentene-1



The yield of styrene from HH-PS (5.2%, nonisothermal degradation 10°C min^{-1}) is low as compared to the yield of styrene from HT-PS (71%, nonisothermal degradation 10°C min^{-1}). This result indicates that HT-PS under these conditions degrades substantially by an unzipping mechansim while, as expected from the structure, HH-PS does not decompose that way but rather by random fragmentation. The structure of chain fragments containing three phenyl rings indicates the evidence of a mechanism of β scission which produces the elements of three monomer units to form 2,3,6-triphenylhexene-1. This type of fragmentation would produce two reactive alkyl radicals which can induce rearrangement of PPO chain according to the following scheme:



Quantitative analysis of the ratio:weight fraction of rearranged dimers to weight fraction of unrearranged dimers showed an increase from 1.96 for pure PPO to 2.56 for PPO degraded in the blend with HH-PS (nonisothermal degradation with the heating rate 10°C min^{-1}). It has been shown in our earlier paper that this ratio approximates the ratio of rate coefficient of rearrangement to rate coefficients of scission[23,29]. The degradation results for the blends of HH-PS–PPO suggest that the radical species formed during decomposition of HH-PS induce rearrangement of PPO. Degradation of PPO in the HH-PS–PPO is also favourable for the formation of higher oligomers of PPO which is indicated by the increase of the ratio:weight fraction of dimers to weight fraction of the monomers. A value 0.74 was found for pure PPO, but a higher ratio of 0.95 was found for the decomposition products of the HH-PS–PPO blend. The influence of PPO on HH-PS decomposition products is minor; the yield of 2,3,6-triphenylhexene-1 is decreased but the yield of 4,5-diphenyl-1,8-octadiene is increased.

For comparison we have also studied briefly the thermal degradation behaviour of one composition of a blend poly(α-methylstyrene)(PMS)–PPO. A single T_g of 186°C had been found previously by dilatometric measurements for a composition of 56% PMS–44% PPO; the blends PMS–PPO were consequently judged compatible. According to t.v.a. (*Figure 8*), PMS decomposes to pure monomer as a result of random initiation of the degradation followed by unzipping to monomer with the depropagating centres being resonance stabilized tertiary radicals. Only slight shifts of the maximum rate temperature of degradation of blends of PMS with PPO (about 18°C) were observed. The temperature of the maximum rate degradation of PPO (440°C) is the same in pure PPO as it is for the blend of PMS with PPO. This relative independence of the degradation of PMS and PPO in their blends indicates that only a weak interaction exists between degrading PMS and PPO. The conclusion that degrading PMS and PPO do not interact was drawn from t.v.a. analysis or from more detailed nonisothermal thermogravimetric studies which will be presented in a separate paper. Noninteraction of PMS with PPO is consistent with the interpretation of the results obtained for thermal degradation of the blend of HT-PS and PPO indicating neither intermolecular nor intramolecular chain transfer is operative during decomposition of HH-PS in these blends.

CONCLUSIONS

Physical blends of HH-PS with PPO were examined by d.s.c. and dilatometry which led to the following conclusions:

(a) The blends form miscible systems over the whole range of composition as indicated by single T_g's found both by d.s.c. and by dilatometry.

(b) At high concentrations of PPO in HH-PS–PPO blends, the blends are on the threshhold of incompatibility as indicated by the increase of the

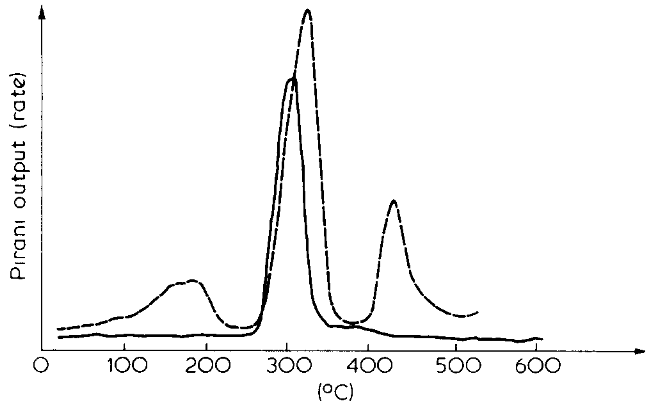


Figure 8 T.v.a. curves for PMS (——) and the mixture 56% PMS–44% PPO (– – –). T.v.a. system with the trap at room temperature

transition width in d.s.c. and the increase of the free volume calculated from dilatometric data.

The investigations of the thermal stability of these blends show some destabilization of PPO by radicals formed during the decomposition of HH-PS. On the basis of product analysis of HH-PS and HH-PS–PPO blends, it is suggested that HH-PS radicals induce rearrangement of PPO.

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