Polymer Bulletin 9, 236-240 (1983)

Polymer Bulletin

Head to Head Polymers

26. Blends of Head to Head and Head to Tail Polyisobutylene

M. Malanga and O. Vogl

Polymer Science and Engineering Department, University of Massachusetts,
Amherst, MA 01003, USA

ABSTRACT

Blends of head to head polyisobutylene and amorphous head to tail polyisobutylene were prepared by casting films of the polymer mixtures from o-dichlorobenzene. The glass transition behavior of the polymer blends was studied by DSC analysis. Two glass transition temperatures were observed over almost the entire composition range which indicates that the two structurally similar head to tail and head to head polyisobutylenes are not miscible even in the molecular weight range of 3000 to 5000.

INTRODUCTION

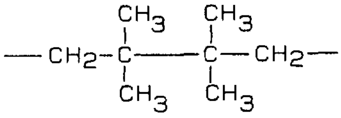
Polymers with head to head (H-H) linkages have recently become available by indirect synthetic routes. Consequently, the characterization of their chemical structure has been carried out and the specific characteristics of the H-H linkages has been studied (MALANGA, et al. 1982).

The blending behavior of selected H-H polymers has also been investigated, primarily by DSC, to determine the miscibility of these H-H polymers with the corresponding regular head to tail (H-T) polymers. By DSC, it was established that H-H polypropylene and H-T polypropylene of moderate molecular weights are miscible (VOGL, YOSHIDA 1980; GROSSMAN, et al. 1981; GROSSMAN 1980). The two glass transition temperatures (T_g) are about 25°C apart. The miscibility of H-H (INOUE et al. 1977) and H-T polystyrene has not been studied because the T_g's of these two polymers are only one degree apart. H-H and H-T poly(vinyl chloride) (PVC), by DSC, were also found to be miscible over the entire range of composition (KONDO et al. 1982) although it was indicated that some broadening of the temperature range of the C_p step was found in one composition range.

Miscibility comparisons were also made of H-H polymers with other polymers that were known to be miscible with the corresponding regular H-T polymers. H-H PVC as well as H-T PVC were found to be miscible over the entire range of blend compositions with poly(ε-caprolactone) (KONDO et al. 1982). H-H polystyrene (PSt) was found miscible with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (KRYSZEWSKI et al. 1982); the complete miscibility of H-T PSt and PPO is the classical example of polymer miscibility.

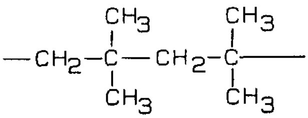
Compatibility of polymers often requires interaction of specific structured units of the polymers as, for example, the phenyl groups in PSt and in PPO. Polymers with only hydrocarbon units in the polymer chain do not show polymer miscibility; it is even known that some polyolefins of widely different molecular weights are not miscible.

It was the purpose of this work to study by DSC the miscibility behavior of H-H polyisobutylene (PIB) and H-T PIB of similar but moderate molecular weight, hydrocarbon polymers with widely different flexibility of the polymer chains.



$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-$$

H-H PIB



$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-$$

H-T PIB

EXPERIMENTAL PART

H-T polyisobutylene (PIB) (Polysciences, Inc.) of M_n of 5200 was used as received.

H-H polyisobutylene (PIB) was prepared by polymerization by Grignard coupling of 2,2,3,3-tetramethyl-1,4-dibromobutane with copper complex catalysts and had a M_n of 3600 (MALANGA 1982).

The thermal transitions in the polymer samples and blends were investigated on a Perkin-Elmer Model DSC-2 Differential Scanning Calorimeter. The temperature scale of the instrument was calibrated with the transition temperature of indium (m.p. 429.78°K) and acetone (m.p. 178.70°K). The weight of each sample was typically 10-30 mg and a heating rate of 20 deg/min and a range of 2 mcal/sec were generally employed.

The DSC scans were used to calculate the glass transition temperatures (T_g) by determining the mid-point of the transition.

To prepare blends of H-H and H-T PIB, both polymers (3000 to 5000 MW) were first dissolved in the solvent (o-dichlorobenzene). The blends were then cast from the warm solvent taking precautions against the H-H PIB precipitating from solution and dried at 0.1 mm.

The DSC traces are shown in Figure 1 and the T_g data presented in Table 1.

Thermogravimetric analyses were performed on a DuPont 900 and 950 analyzer thermobalance. The samples were measured under helium atmosphere with a flow rate of 40 ml/min. Heating rates were 20 deg/min and generally 2.5 to 3.0 mg of samples was used.

RESULTS AND DISCUSSION

The thermal behavior of a series of blends of H-H PIB with H-T PIB were investigated by DSC in the temperature range of -90°C to 130°C. The DSC scans of the blends show a classical dual T_g system over almost the entire composition range which is symptomatic of an incompatible polymer-polymer blend (Table 1).

TABLE 1

Glass Transition Data for Blends of H-H and H-T Polyisobutylene

Blend Sample	T_{g1} (H-T) (°C)	T_{g2} (H-H)
100% H-H	--	85
80%/20% (H-H/H-T)	-55	48
60%/40% (H-H/H-T)	-57	48
40%/60% (H-H/H-T)	-57	45
20%/80% (H-H/H-T)	-59	43
100% H-T	-61	--

Some lowering of the value of T_{g2} H-H PIB was noticed in the blend with 20% H-T PIB. This "plasticization" of the H-H polymer is either real or could be caused by a small amount of low molecular weight material in the H-T sample. After this initial decrease, the T_{g2} of the H-H PIB levelled off (Figure 1).

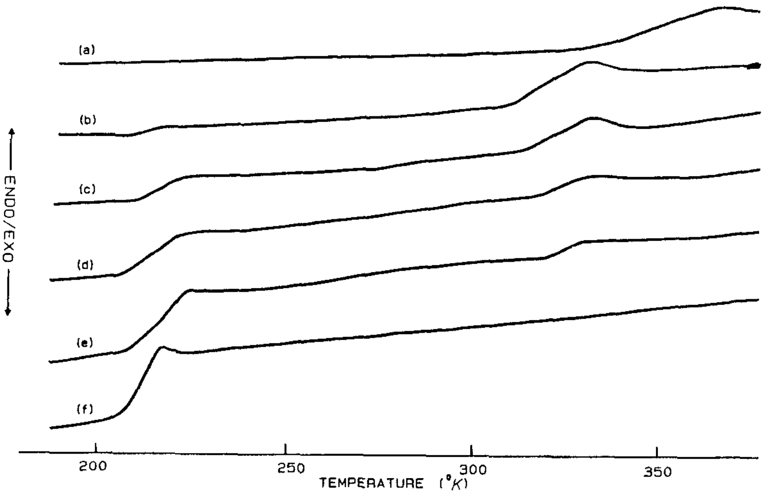


Figure 1: DSC scans for blends of H-H with H-T polyisobutylene; (a) 100% H-H; (b) 80:20, H-H:H-T; (c) 60:40, H-H:H-T; (d) 40:60, H-H:H-T; (e) 20:80, H-H:H-T; (f) 100% H-T. Scans from -90 to +100°C at 20°/min.

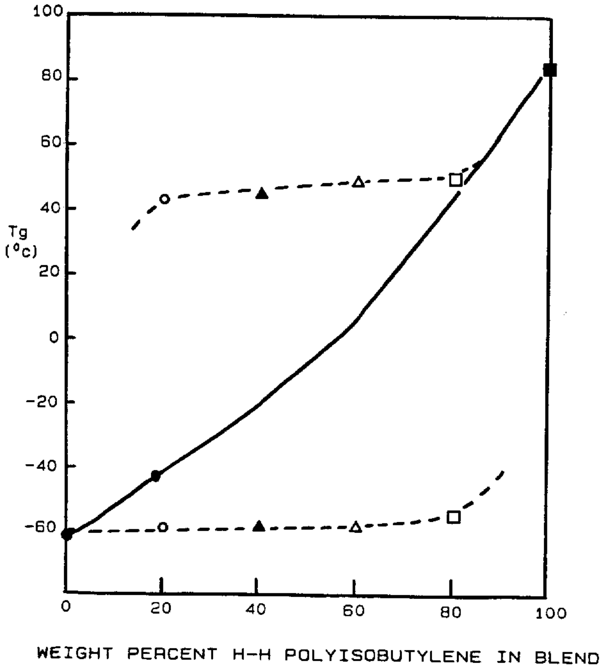


Figure 2: T_g vs. weight percent H-H polyisobutylene in the blend. ■ 100% H-H; □ 80:20, H-H:H-T; △ 60:40, H-H:H-T; ▲ 40:60, H-H:H-T; o 20:80, H-H:H-T; ● 100% H-T.

---- Experimental

____ Calculated by Fox-Flory equation.

Figure 2 shows the plot of T_g as a function of weight percent H-H PIB in the blend. The broken lines indicate the experimental results of the study, while the solid line shows the values calculated from the Fox-Flory equation. The theory (FOX, FLORY 1948) predicts that for a completely compatible system a single T_g will be found for the blend; the position of the T_g is based on the weight percent of each component.

The TGA study of the thermal degradation of the blends of H-H PIB and H-T PIB also indicates immiscibility (Figure 3). The two homopolymers degrade independently of each other and also do not cause a decrease of the degradation temperatures. The results can be interpreted by assuming that the degradation (MALANGA 1982) occurs primarily through tertiary radicals and only a few primary radicals are involved in the degradation.

When both the DSC and TGA studies of the blends for H-H and H-T PIB are taken together a strong case for the incompatibility of H-H PIB and H-T PIB can be made. It is interesting that an example is found where two polymers of identical chemical composition and even moderate molecular weight but with somewhat different chemical structure do not interact with each other favorably enough to form a single phase.

Our investigations of the properties of H-H PIB and H-T PIB have shown large differences in thermal properties and crystallinity by simply arranging the geminal dimethyl substituents in the polymer backbone in 1,2 rather than 1,3 position. This structure caused H-H PIB to have a much stiffer chain and to be incompatible with H-T PIB.

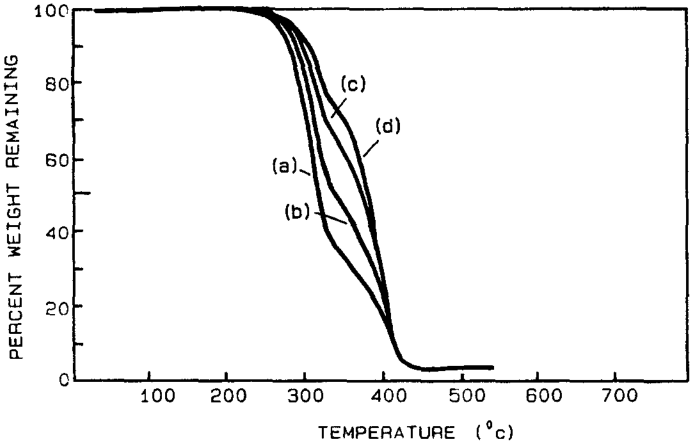


Figure 3: TGA for blends of H-H with H-T polyisobutylene. (a) 80:20, H-H:H-T; (b) 60:40, H-H:H-T; (c) 40:60 H-H:H-T; (d) 20:80, H-H:H-T. Heating Rate, 20°/min, flow rate of 40 ml/min helium.

ACKNOWLEDGEMENTS

The work was in part supported by the ACS Petroleum Research Fund, No. 13047-AC7, and the Materials Research Laboratory of the University of Massachusetts.

REFERENCES

1. FOX, T.G. and FLORY, P.J., J. Amer. Chem. Soc., 70, 2384 (1948).
2. GROSSMAN, S., Ph.D. Dissertation, University of Massachusetts, 1980.
3. GROSSMAN, S., STOLARCZYK, A. and VOGL, O., Monatsh. Chem., 112, 1279 (1981).
4. INOUE, H., HELBIG, M. and VOGL, O., Macromolecules, 10, 1331 (1977).
5. KONDO, T., KITAYAMA, M. and VOGL, O., Polymer Bulletin, 8, 9(1982).
6. KRYSZEWSKI, M., JACHOWICZ, J., MALANGA, M. and VOGL, O., Polymer (London), 23(2), 271 (1982).
7. MALANGA, M., Ph.D. Dissertation, University of Massachusetts, 1982.
8. VOGL, O., MALANGA, M. and BERGER, W., ACS Monograph, in press.
9. VOGL, O. and YOSHIDA, S., Preprints of the 41st. Annual Meeting, Japan Chem. Soc., Higashiosaka, 131 (1980).

Accepted December 9, 1982