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Free Volume of cis-1,4 polyisoprene/polybutadiene blends

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Summary

The number and radius of molecular order free space present in polybutadiene (PBD)/polyisoprene (PIP) blend were observed by positron life-time measurement, and apparent free volume fraction was estimated. The changes in the number and radius of the free space were not represented to be a linear function of blend composition. The apparent free volume fraction increased by mixing PBD with PIP and was approximated by a concave curve depicted against blend composition, even though the excess volume of mixing was proved to be negative. The change in the apparent free volume fraction was related to the variation of thermal expansion coefficient on blend composition.

Introduction

High molecular weight rubber is, in general, immiscible with dissimilar polymers (1). However, *cis*-1,4 polyisoprene (PIP) forms miscible mixtures with polybutadiene (PBD) in relatively high 1,2-isomeric unit content (2, 3). At just 32.3% 1,2-unit content, LCST phase behavior of the blend has been found (3-6). In the case of high molecular weight polymer-polymer blends, the combinatorial entropy contribution is small and is usually negligible. Therefore, the formation of one-phase state of the PBD/PIP blend have provided insoluble problem because it is predicted only the dispersion force as an intermolecular interaction. In our previous studies, volume contraction which has significant effect on change in free energy of mixing and conformational change of PBD and PIP on mixing has been found in the one phase region in PIP/PBD blend at 25°C (7-11). It is considered that they relate to free volume changes of PBD and PIP on mixing. However, the change in free volume has not been observed in the blend.

Ortho-positronium (o-Ps) is an effective prove to estimate the free volume size and fraction present in amorphous region of polymers since the life-time and intensity of o-Ps are proved as corelation with average size and fraction of free volume, respectively. For this purpose, positron annihilation life time measurement has been used (12). Recently, the miscible Polystylene/ Poly(tetra methyl carbonate) blends was reported to show a contracting of free volume fraction while immiscible Polystyrene/polycarbonate blends a complicate variation (13). In this study, a free volume of PBD, PIP and their blends is observed by the positron annihilation life-time measurement.

Experiments

PIP ($\overline{M}_w$=7.3x10^5, $\overline{M}_w/\overline{M}_n$ =1.84) and PBD ($\overline{M}_w$=2.14x10^5, $\overline{M}_w/\overline{M}_n$=1.03) is supplied from Nippon Zeon Co., Ltd.. Microstructure obtained by ^{13}C-NMR and infrared spectroscopy was 30.5% *cis*-1,4, 37.2% *trans*-1,4 and 32.3% 1,2 linkages for PBD and 98.9% *cis*-1,4, 0.7% *trans*-1,4, 0.4% 3,4 and undetectable amount of 1,2 linkages for PIP. PIP and PBD were weighted to desired blend ratios and dissolved in toluene. The solution was poured into methanol. The precipitated samples were dried *in vacuo* at 40□ for a week. The PIP and PBD samples were prepared by same procedure. 1mm thick specimen were used since the penetration of <546 keV positrons emit from ^{22}Na nuclei in ordinary polymers were less than 1mm. All measurements were performed at 23.5±0.5 □.

The positron source was 7x10^5 Bq of ^{22}NaCl, deposited on a 1 µm Kapton foil folded. The source was sandwiched between two identical specimen and positron annihilation life-time was measured by a high efficiency fast-fast coincidence measuring system with BaF_2 scintillation attached to XP2020Q (Phillips) photomultiplier tubes. The time resolution of the system was □230 ps (full width at half maximum, FWHM). The annihilation curves of positrons were measured at 25 □ for 2days to collect approximately 3x10^6 counts. The curves were decomposed into four components by POSITRONFIT (14) computer program with the fitting performance expressed as the least squares less than 1.2. Inverse Laplace transformation by using CONTIN computer program is applied to decay curves in order to obtain distribution function (15).

Results and Discussion

The decay curve of positron annihilation for amorphous polymers is usually resolved into three or four life time components (16). The standard variation of data are τ_1: ±0.01ns, τ_2: ±0.02ns, τ_3:±0.02ns, τ_4:±0.02ns and I_1:±5%, I_2:±5%, I_3:±3%, I_4: ±0.5%. The shortest components, τ_1: □160ps, is well-known to be combined to self annihilation of para-positronium (p-Ps) and free annihilations of positron. The second shorter components, τ_2: □400ps, is attributed to annihilation of positrons trapped in various vacancies and free volumes present in amorphous regions, respectively. The longest τ_4: □2 ns and its relative intensity I_4 are associated with pick-off annihilation of o-Ps.

A simple quantum mechanical model discussion provided by Jean shows a semiempirical equation between the measured o-Ps life time (τ_4) and the free volume hole radius (R) was proposed as follows (17).

$$\tau_4 = \frac{1}{2}\left[1 - \frac{R}{R+0.166} + \frac{1}{2\pi}\sin\frac{2\pi R}{R+0.166}\right]^{-1} \quad (1)$$

where τ_4 and R are expressed in ns and nm, respectively. In Figure 1, the variation of size of free volume, represented as free volume radius, against the blend composition is shown. It is clearly shown that the free volume radius of the PBD/PIP blend was larger than that of PBD or PIP, despite that the values of free volume radius contained significant error. On the other hand, the quantity of free volume represented as I_4 increased with the addition of PBD, as shown in Figure 2. Both the radius and fraction of free volumes were not proportional to the blend composition. This demonstrates that the additivity of free volumes is not applied to the mixture of PBD with PIP.

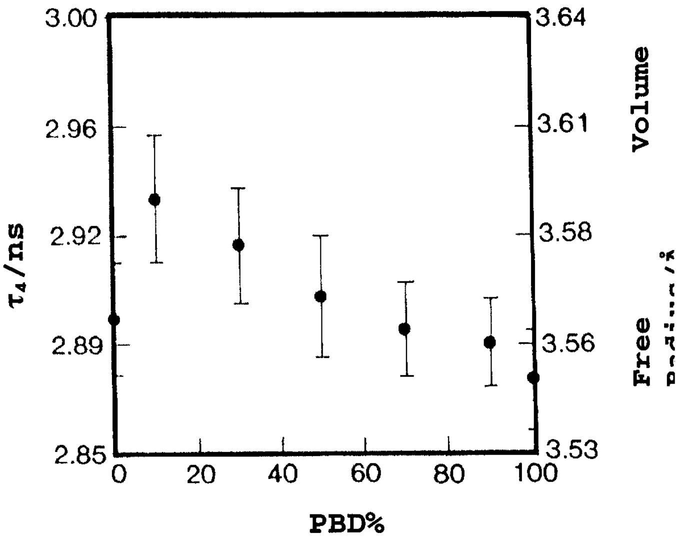

Figure 1τ_4 and free volume radius of PBD, PIP and their blends.

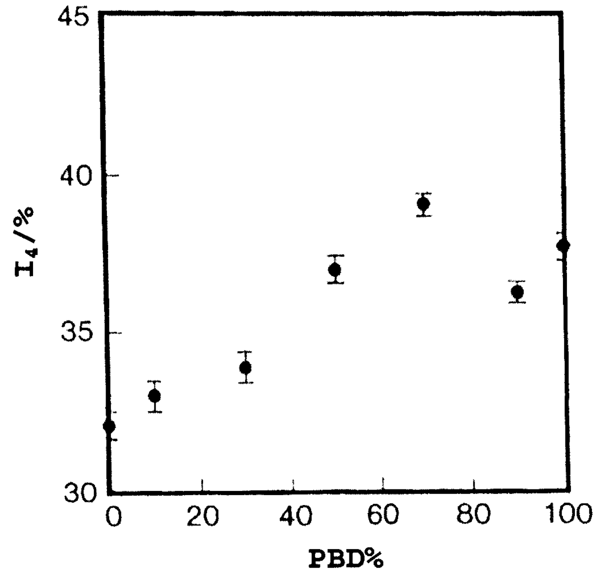

Figure 2 I_4 of PBD, PIP and their blends.

The apparent free volume fraction of PBD, PIP and their blends was estimated by Nakanishi and Jean expression (12) from radius and fraction of free volume. Excess of the apparent free volume fraction (f_{app}), expressed as the multiplication of sphericized free volume size (V_f) and I_4, $f_{app}=V_f(AI_4+B)$, from additive role is shown against blend composition in Figure 3, where V_f was calculated from R and by putting A=1 and B=0. A and B might be estimated on the basis of any physical model or the other physical properties after the establishment of the exact size and shape of free volumes. However, it is impossible to determine them independently at present time, so that A and B are approximated to be 1 and 0 because we would compare a relative variation of each f_{app}. The f_{app} was approximated by a concave curve depicted against blend composition. This concave curve nature in f_{app} makes us to expect a positive change in excess volume of mixing. However, in our previous work (14), the excess volume of mixing of PBD/PIP blend has been found to be negative at 25 ℃. If the positive change of f_{app} on mixing occurs exactly in the blend, the positive change in f_{app} and negative change in excess volume of mixing have to be taken into account in the theoretical treatment. It is noted that there are the serious error and ambiguous assumption to estimate the f_{app} by positron life-time measurement.

In order to ensure the positive change in the f_{app} on mixing, thermal expansion coefficients at 25 ℃ for various PBD/PIP blend and their homopolymers, which were measured in our previous study (10) is shown in Table 1. The thermal expansion coefficients of the blends were significantly larger than those of homopolymers. The thermal expansion coefficient represents an ability of thermal expansion of the polymer. This implies that the thermal expansion coefficient is proportional to the free volume fraction. The increase in thermal expansion coefficient by blending, thus, suggests the positive change in f_{app} on mixing.

Heffner and Mirau (18) showed that methyl group of *cis*-1,4 polyisoprene was close to vinyl group of 1,2 polybutadiene by mixing. We predicted the presence of miscible stable structure on the basis of volume contraction on mixing and NMR-T1 change on

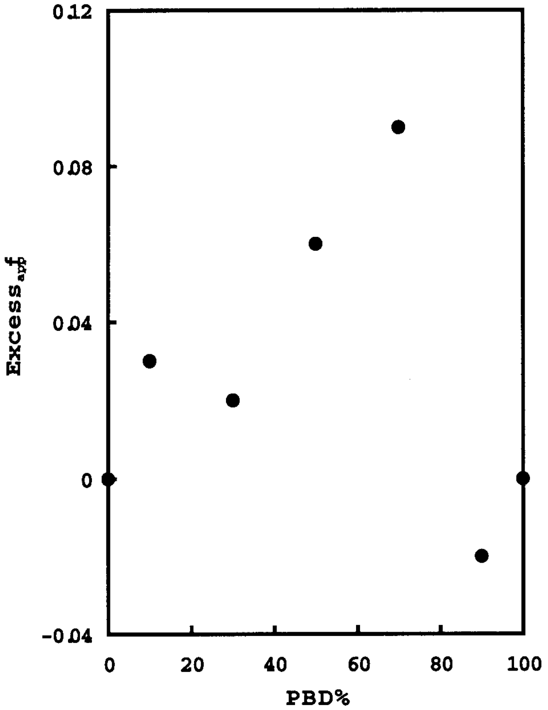

Figure 3 Composition dependence of free volume fraction of PBD/PIP blends.

Table 1 Thermal expansion coefficient at 25 °C of PBD, PIP and their blends.

PBD/PIP (v/v)	α/K^{-1}
0/100	$7.052x10^{-4}$
30/70	$7.148x10^{-4}$
50/50	$7.087x10^{-4}$
60/40	$7.363x10^{-4}$
70/30	$7.239x10^{-4}$
100/0	$7.063x10^{-4}$

mixing (10). The estimated negative volume of mixing was about 0.3%, showing relatively small volume contraction on mixing. If PIP was attracted strongly with PBD, the volume of the blend could contract more significantly. The increase in the apparent free volume fraction may be explained to be due to the strong intermolecular interaction between PIP and PBD and the slight volume contraction on mixing. This demonstrates that the specific miscible structure is formed by the strong intermolecular interaction which overcomes the loss of entropy of mixing. In our subsequent study, the miscible stable structure and the true interaction between PIP and PBD will be shown.

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