



Selective determination of glass transition temperature and vibrational properties at the chain end of polystyrene by Fourier transform infrared measurement in combination with deuterium-labeling



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ABSTRACT

Glass transition temperature (T_g) and vibrational properties at the chain end of polystyrene (PS) were selectively determined by a novel method utilizing Fourier transform infrared (FT-IR) spectroscopy. In this method, PSs having almost the same number average molecular weight (M_n) but selectively deuterated at different sites, midchain (M-PS, $M_n = 10.7$ kDa) or chain end (E-PS, $M_n = 10.3$ kDa), were synthesized and the asymmetric stretching vibration of the main chain CD_2 ($\nu_{as}(CD_2)$) were analyzed in detail. We found that the temperature dependence of the $\nu_{as}(CD_2)$ frequency shows a clear inflection at the calorimetric T_g of PS. The inflection temperature was defined as $T_{g,FTIR}$, which represents the T_g at the local region around the deuterated sites. Although *higher* segmental mobility at the chain end had been shown *above* the T_g in our earlier work, this study found that the $T_{g,FTIR}$ s of the M-PS and E-PS are the same. From this result, it was concluded that the chain ends move cooperatively with numerous neighboring other segments, averaging out those mobilities at temperatures around the T_g . On the other hand, the $\nu_{as}(CD_2)$ frequency of the E-PS was by a few cm^{-1} higher than that of the M-PS for any temperature. This was explained in terms of the discontinuity of the repeat unit at the chain end resulting in reduced interactions between repeat units along the chain.

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1. Introduction

The chain end is common and unique local structure of polymers; the chain end often affects the physical properties of polymeric materials. For example, it is well-known that the chain ends act as plasticizers; therefore, the glass transition temperature, T_g , of a polymer decreases with an increase in the concentration of the chain end [1–3]. In addition, the chain ends tend to locate at the surface and interface regions of polymeric materials; therefore, they often dominate the properties of such local regions [4–8]. For example, Kajiyama et al. showed the segregation of the PS chain ends into the surface of a film and they proposed that this is the major origin for the local decrease in the T_g at the film surface [6]. Therefore, understanding the properties of the chain end will be

important for tuning properties of nano-scale materials, such as nanocoatings, nanocomposites, nanoparticles, etc. which have large extent of the surface or interface regions.

Labeling techniques are powerful and advantageous to study the local properties of the chain end; photo-labeling [9,10], fluorescence-labeling [11,12], spin-labeling [13–16], deuterium-labeling [17–19], and cyano-labeling [20–24] have been applied. In particular, the segmental mobility at the chain end of the PS in the bulk state has been intensively and quantitatively studied by Lund et al. [22–24] using dielectric spectroscopy with the cyano-labeling and by Miwa et al. [13,14,16] using electron spin resonance (ESR) spectroscopy with spin-labeling. The segmental motion detected by these techniques is the α relaxation mode of a PS and the time scale is $\approx 10^{-6}$ s around $T_g + 50$ K. These studies revealed that the segmental mobility at the chain end is roughly double compared to that at the midchain sites at $T_g + 50$ K because of reduced intermolecular constraint and higher degree of freedom

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in motion at the chain end. Moreover, the dielectric study showed that the difference between the segmental mobilities at the chain end and the midchain sites decreases as temperature approaches to the T_g , and the difference virtually vanishes at the T_g [22]. This result was supported by the ESR study where no difference between the T_g s sensed by the label agents attached at the chain end and the midchain sites is shown [16]. However, one may suspect that these results could be artificial because the chain ends of the PSs were modified with a strong polar group, $C\equiv N$, and a relatively large labeling molecule, 2,2,6,6-tetramethyl-4-piperidine-1-oxyl (TEMPO), in the dielectric and ESR techniques, respectively. That is, nobody knows how much the original nature of the chain end is disturbed by the $C\equiv N$ and TEMPO. At this point, the deuterium-labeling is much superior to the above two techniques and the disturbance to the original nature of the chain end is as little as possible [17–19]. In the present work, we propose a novel technique to selectively determine the T_g at the local region around the chain end of the PS utilizing Fourier transform infrared (FT-IR) spectroscopy in combination with the deuterium-labeling.

Very recently, the authors selectively determined the stretching vibration at the chain end of the PS using FT-IR spectroscopy [19]. The FT-IR is generally applied to evaluate chemical interactions, such as van der Waals interaction, hydrogen bonding, dipole–dipole interaction, etc. because the vibrational frequencies of chemical bonds are generally sensitive to the chemical interactions [25–27]. In the work, PSs selectively deuterated at the chain end or midchain sites were prepared and the frequency of the stretching vibration of the aliphatic C–D was measured. The authors found that the stretching vibration frequency at the chain end is higher compared to that at the midchain site even in the glassy bulk state. This result revealed that interactions between repeat units along the chain are locally reduced at the chain end because of the discontinuity of the repeat unit.

Focusing on polymers, sensitivities of the frequency and intensity of FT-IR bands to relaxation phenomena have been also utilized. For example, plots of peak frequency or intensity vs. temperature displayed an inflection point near the T_g [28–42]. In the present study, temperature dependences of the frequency and band shape of stretching vibrations of the main chain CD_2 group located to the chain end and midchain site of the PS have been analyzed. It is well-known that non-deuterated CH_2 stretching vibrations of the alkyl chain are sensitive to conformational structures; therefore, these bands are utilized to detect the melting and liquid crystalline transitions [43–47]. The stretching vibrations of the main chain CD_2 group are also expected to be conformationally sensitive and effective to detect the glass transition of the PS. In the present work, the T_g at the local region around the deuterated sites (midchain or chain end) of the PS is selectively determined from the temperature dependence of the stretching vibration frequency of the main chain CD_2 . Moreover, the effect of the number average molecular weight on the T_g at the local region around the chain end is also examined.

2. Experimental section

2.1. Sample preparations

2.1.1. Materials

Inhibitors in styrene (ST, Extra Pure Reagent, Nacalai Tesque Co., Ltd.) were adsorbed on activate aluminum oxide (Kanto Chemical Co., Inc.) and removed before use. β,β -deuterated styrene (D2-ST, 99%, CDN Isotopes Inc.), tributyltin hydride (97%, Merck Co., Ltd.), N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA, 99%, Tokyo Chemical Co., Ltd.), 1-phenylethyl bromide (1-PEBr, 95%, Tokyo Chemical), and CuBr (98%, Nacalai) were used as received. Anisole

obtained from Nacalai was dehydrated using a molecular sieve (3A, Kanto Chemical). Toluene (Kanto Chemical Co., Ltd., Extra Pure Reagent), methanol (Kanto Chemical, Extra Pure Reagent), and chloroform (Kishida Chemical Co., Ltd., Extra Pure Reagent) were used without further purification.

2.1.2. Preparation of deuterium-labeled PS

Two PSs having almost the same molecular weight but labeled with D2-ST at different sites, midchain or chain end, were prepared using atom transfer radical polymerization (ATRP) (Fig. 1). The notations for the midchain-labeled and end-labeled PSs are M-PS and E-PS, respectively. In our previous work, the PSs labeled with α,β,β -deuterated styrene (D3-ST) at the midchain or chain end were synthesized and the procedure was described in detail [19]. The M-PS and E-PS were synthesized with the same procedure using the D2-ST instead of the D3-ST. For the M-PS, 2 mol% of the D2-ST was randomly copolymerized with ST; therefore, the deuterated sites are located randomly along the chain. Because the M-PS and E-PS were synthesized using ATRP, the chain end was terminated with a bromine. In the present work, the bromine at the chain end was exchanged to a hydrogen by the reaction with tributyltin hydride [48]. The number average molecular weight (M_n) and the polydispersity index (M_w/M_n) for the M-PS determined by gel permeation chromatography (GPC) are 10.7 kDa and 1.23, respectively. On the other hand, the M_n and M_w/M_n for the E-PS are 10.3 kDa and 1.22, respectively. A non-deuterated PS (Fig. 1(C)) was also prepared, and the M_n and M_w/M_n are 10.3 kDa and 1.23, respectively.

2.1.3. Preparations of binary blends

Binary blends of the deuterium-labeled PS (M-PS or E-PS) with an oligomer PS were prepared. The oligomer PS ($M_n = 950$ Da, $M_w/M_n = 1.10$) purchased from Tosoh Co., Ltd is denominated PS950. Firstly, the labeled PS and PS950 were dissolved in chloroform with a concentration of 5 wt%. The solution was casted on a Teflon plate and dried in the hood for one day, and then the residual solvent in the sample film was completely removed in a vacuum at 373 K for 24 h. The M_n s for the deuterium-labeled PS/PS950 (60/40) and (70/30) blends are calculated to be ca. 2.1 kDa and 2.6 kDa, respectively.

2.2. Measurements

2.2.1. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra were recorded with a Perkin–Elmer Spectrum100 FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The measurements were performed on the transmittance mode at 2 cm^{-1} optical resolution with a minimum of 128 scans. The PS film was prepared on a KBr plate and inserted into a custom-

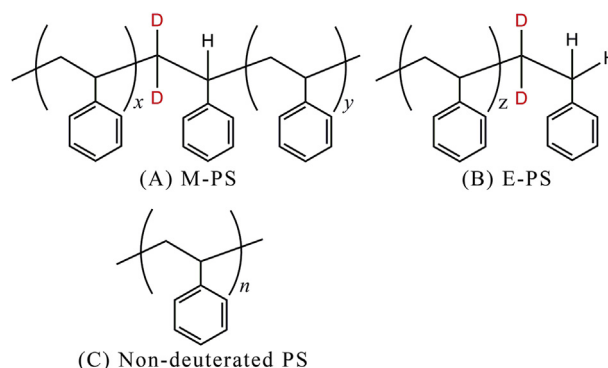


Fig. 1. Chemical structures of deuterated PS at midchain (A) and chain end (B). Non-deuterated PS is shown in (C).

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