

CONFORMATIONAL RELAXATION OF STYRENE-BUTADIENE RUBBERS HAVING A DIFFERENT MICROSTRUCTURE BUT THE SAME COMPOSITION AT HYDROPHILIC AND HYDROPHOBIC INTERFACE

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ABSTRACT

The orientational relaxation of poly(styrene-*r*-butadiene) (SBR) chains at solid interfaces were examined by sum-frequency generation spectroscopy (SFG) with the molecular-level depth resolution. To tackle an effect of interaction between segments and substrate on the interfacial mobility of chains, SBRs having different microstructures but the same composition, were prepared on hydrophilic and hydrophobic quartz substrates. At a hydrophilic interface, SFG signal intensity from phenyl groups decreased with increasing temperature and the temperature dependence markedly changed at a characteristic temperature (T_c). The T_c , in which chains start to structurally relax, was ca. 150 K higher than the bulk glass transition temperature. It is likely that 1,2- and 1,4-butadiene are energetically comparable to each other for the quartz surface. On the other hand, the T_c was not discerned at a hydrophobic interface. This makes it clear that the orientational relaxation was markedly suppressed possibly due to the stronger interaction between chain segments and hydrophobic surface.

INTRODUCTION

Polymer nanocomposites, in which inorganic nanofillers are dispersed, show better mechanical and dielectric properties than the neat polymer matrix. The improvement of the properties strongly depends on the aggregation states and molecular motion of chains at the interface with the filler. So far, based on sum-frequency generation (SFG) spectroscopy, we reported that adsorbed polymer chains in direct contact with the solid surface were frozen in mobility up to a temperature far above the bulk glass transition temperature (T_g^b), depending

on the interaction between them.¹⁻³ Given that the interaction became stronger, the reinforcement effect should be more effective, leading to better mechanical properties. The objective of this study is to obtain better understanding of how the interaction between polymer and solid surface impacts the polymer mobility at the interface.

EXPERIMENTAL SECTION

As samples, poly(styrene-*r*-butadiene) (SBR) composed of constant styrene (St) content (22–24 mol%) and varying 1,2- and 1,4-butadiene (1,2- and 1,4-Bd) contents were used. Table 1 shows a number-average molecular weight (M_n), molecular weight distribution (M_w/M_n), T_g^b and the molar ratio of St and 1,2-Bd of the samples. As hydrophilic and hydrophobic substrates, fused quartz without/with a chloro(decyl)dimethylsilane (DDS) coating monolayer was used. SBR films were prepared on the substrates by a spin-coating method from toluene solutions. Then, SBR films prepared onto a quartz prism and a quartz window were adhered in the surface-to-surface geometry at ($T_g^b + 80$) K under vacuum for 24 h. SFG spectra were collected with visible and tunable infrared beams traveling through a prism and overlapping at the SBR/solid interface. The measurements were carried out with a polarization combination of *s**s**p* (SF output, visible input and infrared input).

Table 1: Characteristics of SBRs.

Sample	M_n	M_w/M_n	T_g^b / K	St in SBR / mol%	1,2-Bd in Bd / mol%
SBR28	200k	1.08	233	22	28
SBR44	190k	1.04	245	22	44
SBR69	160k	1.10	266	24	69

RESULTS AND DISCUSSION

Figure 1(a) shows SFG spectra for SBR28, SBR44 and SBR69 films at the quartz substrate. A peak observed at $2,846\text{ cm}^{-1}$ was assigned to the symmetric C-H stretching vibration of methylene groups (CH_2s). A peak observed at $2,905\text{ cm}^{-1}$ could be assigned to the anti-symmetric C-H stretching vibration of methylene groups (CH_2as) and/or the C-H vibration

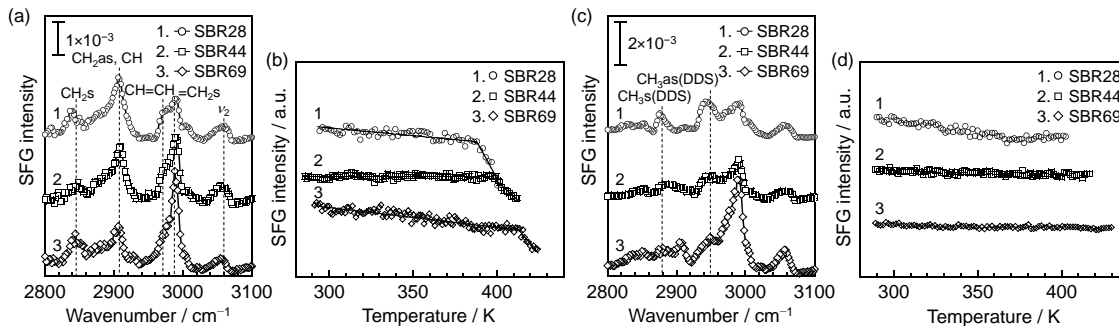


Figure 1: SFG spectra for SBR28, SBR44 and SBR69 at (a) quartz and (c) DDS-treated quartz interface, respectively. Temperature dependence of SFG peak intensity of ν_2 mode in phenyl group at (b) quartz and (d) DDS-treated quartz interfaces, respectively.

of methyne groups (CH). Peaks at 2,972 and 2,988 cm^{-1} were assigned to the C-H stretching vibration of vinylenes groups (CH=CH) in 1,4-Bd and the C-H stretching vibration of vinyl methylene groups in 1,2-Bd (=CH₂s), respectively. Also, a peak at 3,060 cm^{-1} was originated from the ν_2 mode of phenyl groups. Taking into account that SFG signals can be obtained from functional groups orientated at the interface, the above results indicate that the local conformation of SBR chains was ordered at the quartz interface even at a temperature above the T_g^b . Also, it is noteworthy that the signal intensity for =CH₂s increased with increasing 1,2-Bd content in SBR.

To examine the orientational relaxation of SBR at the interface, the signal intensity of the ν_2 mode was chased during the heating process. Figure 1(b) shows temperature dependence of signal intensity at 3,060 cm^{-1} . In the case of SBR28, the intensity gradually decreased with increasing temperature, and the slope remarkably changed at 388 K, at which the local conformation of interfacial chains started to alter. This characteristic temperature T_c was comparable to those based on the SFG signals from CH=CH and =CH₂s. Thus, it seems most likely that the orientational randomization resulted from the segmental motion of SBR chains. The difference between T_c and T_g^b was approximately 150 K. This makes it clear that the mobility of SBR chains was strongly suppressed in close proximity to the quartz interface. A similar trend was also observed for SBR44 and SBR69.

To examine how the surface chemistry of the substrate impacts the interfacial mobility, similar experiments were conducted at the hydrophobic DDS-treated quartz interface. Figure 1(c) shows SFG spectra for the SBR films at the DDS-treated quartz interface. In addition to the peaks originated from SBR, peaks assignable to the symmetric and anti-symmetric C-H stretching vibration of methyl groups (CH₃s, CH₃as) for DDS were observed. Figure 1(d) shows the relationship between temperature and peak intensity of the ν_2 mode. Although a gradual decrease in the SFG intensity was discerned, the slope remained almost changed. This means that the orientational relaxation of SBR chains at the interface did not occur within the temperature range employed. A possible explanation for this finding is that the interfacial relaxation was not allowed due to the stronger interaction between SBR chains and the hydrophobic surface. Thus, it can be claimed that the interaction of segments with a solid surface strongly impacts the segmental mobility at the interface.

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