Nuclear Magnetic Resonance Relaxation in Random and Block Copolymers of Styrene and Butadiene

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Received October 26, 1970

ABSTRACT: The proton spin–lattice relaxation of several butadiene–styrene copolymers has been studied over the temperature range between −50 and 200°. The butadiene and styrene segments of random copolymers participate in concerted motions, the frequency of which decreases with increasing amounts of styrene. Local chain motions in the butadiene and the styrene domains of butadiene-rich block copolymers are similar to the corresponding motions in the bulk homopolymers. However, striking changes in chain mobility within butadiene domains were observed when the styrene content became very large.

Nmr techniques have been widely used to study molecular motion in bulk homopolymers.[1-3] Fewer nmr studies of copolymers have been reported; studies using composition as a variable are particularly sparse.[4] This is rather surprising, for it seems natural to ask how the motions of the comonomers change when they are diluted in one another. One could also ask how chain mobility is influenced by the spatial arrangement of the two components; *i.e.*, how does local motion in a random copolymer differ from that in a block copolymer of the same overall composition? The present work is a preliminary attempt to deal with these questions; we studied molecular motion in random and block copolymers of styrene and butadiene.

Experimental Section

Random styrene–butadiene copolymers were synthesized by emulsion polymerization.[5] The reactions were taken to low conversion (10–20%), in order to ensure chemical uniformity throughout the products. The relative amounts of styrene and butadiene in these materials were determined by infrared analysis. Diblock copolymers of styrene and butadiene were obtained through the courtesy of Dr. Gunther Molau, Dow Chemical Co. They were found to contain between 20 and 75% polybutadiene, with most of the polybutadiene arranged in trans sequences (infrared analysis). Variations in the polystyrene content produced no significant changes in the relative amounts of *cis*- and *trans*-polybutadiene.

The nmr spin–lattice relaxation of these samples was studied over the temperature range between −50 and 200°. T_1, the spin–lattice relaxation time, was determined by the 180–90° pulse technique on a Brucker pulsed spectrometer operating at 36 MHz. The null method was used.[6] Pulse lengths ranged between 2 and 4 μsec.

Results and Discussion

The present results should be viewed in light of previous T_1 measurements on the polystyrene and polybutadiene homopolymers. Slichter and Davis[7] studied the proton T_1 of *trans*-polybutadiene as a function of temperature. Their data show a single T_1 minimum, occurring in the neighborhood of 0°, which they attribute to the polybutadiene glass transition viewed at a frequency of 20 MHz. Several groups[8-10] have reported T_1 studies of polystyrene as a function of temperature. There is a single T_1 minimum in the neighborhood of 180–200°. Presumably this reflects the glass transition of polystyrene viewed at megahertz frequencies.

Figure 1 shows T_1–temperature plots for three random styrene–butadiene copolymers of various compositions. Each sample exhibits a single T_1 minimum, the temperature of which increases with increasing styrene content. Note also that these T_1 minima occur at temperatures lying between those of the polystyrene and polybutadiene homopolymers. The implications of these findings are clear. Random copolymerization places the styrene and butadiene units in close contact with one another. In this arrangement, the motions of both units are strongly coupled, giving rise to a single T_1 minimum. The rate at which this concerted process occurs decreases with increasing amounts of the bulkier styrene.

Contrast these results with those observed for the styrene–butadiene diblock copolymers (Figure 2). The T_1–temperature curves for samples containing less than 50% styrene are extremely similar and appear to be the weighted superposition of T_1–temperature plots for the polybutadiene and polystyrene homopolymers. This should not be surprising. The components of block copolymers are known to segregate into domains. Nuclear relaxation, which is sensitive to local chain motions and relatively insensitive to longer range motions, could be expected to view such a material as almost a physical mixture of the two homopolymers. On this basis, it is interesting to note that the local chain motions in both domains of butadiene-rich block copolymers are indistinguishable from local chain motions in the bulk homopolymers.

Figure 2 shows that the low-temperature T_1 minimum shifts to higher temperatures as the styrene content increases beyond 50%. Since we attribute this minimum to the motion of polybutadiene segments, these shifts indicate that this motion is impeded as the polystyrene content becomes very large. Undoubtedly this has something to do with reversal between majority and minority components and with bringing a larger fraction of the polybutadiene segments into closer proximity with the segments of polystyrene. This can also be viewed in terms of thermal expansion. Recall that T_1 is commonly measured as a function of temperature at constant

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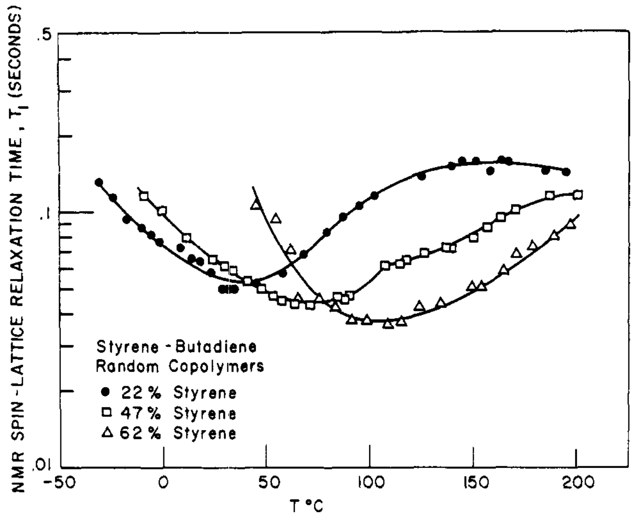

Figure 1. Proton spin-lattice relaxation of various styrene–butadiene random copolymers plotted as a function of temperature.

pressure. Under these conditions, the observed increase in molecular mobility with increasing temperature is related to two factors: (A) the increased thermal energy of the chain segments and (B) the thermal expansion of the entire sample, which gives the individual segments more room to move. T_1 studies as a function of pressure indicate that the latter effect is quite sizable:[11,12] T_1 minima would occur at appreciably higher temperatures if T_1-temperature studies were carried out at constant volume rather than at constant pressure. These observations have relevance in the present studies, for one comes close to doing a constant volume experiment when examining motion in polybutadiene domains imbedded in a matrix of glassy polystyrene. Since the expansion of polystyrene below its T_g is much less than that of bulk polybutadiene above its T_g, the shifts in the temperatures of the T_1 minimum might be explained on this basis.

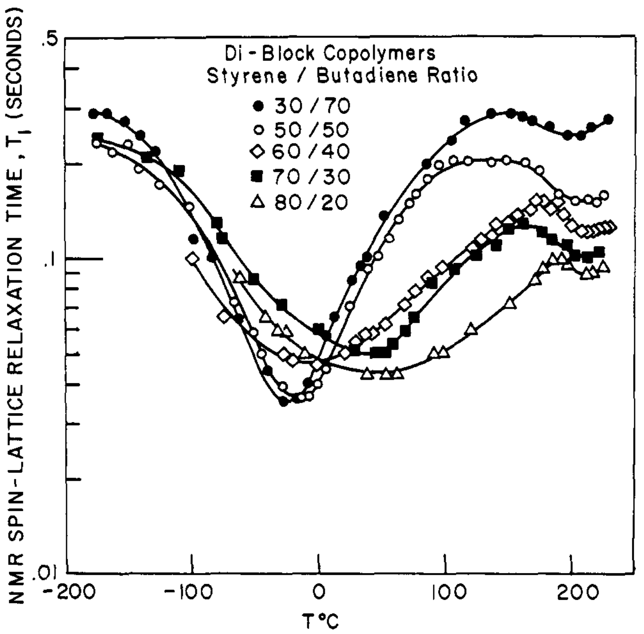

Figure 2. Proton spin-lattice relaxation of various diblock styrene-butadiene copolymers.

Unsuccessful attempts were made to change the mobility within the block copolymers through chemical and thermal pretreatments. A number of samples were examined after reprecipitation from benzene, methyl ethyl ketone, and 4-heptanone—solvents that have varying interaction with polybutadiene and polystyrene. Other samples were maintained at 120° (above the T_g of polystyrene) for 1 hr. Half of these samples were quenched to Dry Ice temperatures, while the remainder were allowed to cool slowly. The T_1-temperature data on all these pretreated samples were indistinguishable from corresponding measurements made on the original materials.

Acknowledgment. We are grateful to Dr. Gunther Molau, Dow Chemical Co., who supplied the block copolymers used in this study.

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