A Dielectric Study on Dynamics of Tethered Ciiains: Styrene-Isoprene Diblock Copolymers in Bulk and in Selective Solvent

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A DIELECTRIC STUDY ON DYNAMICS OF TETHERED CHAINS: STYRENE-ISOPRENE DIBLOCK COPOLYMERS IN BULK AND IN SELECTIVE SOLVENT

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ABSTRACT

We examined by dielectric spectroscopy the dynamics of cis-polyisoprene (I) blocks tethered on glassy polystyrene (PS) domains in microphase separated styrene-isoprene (SI) diblock copolymers in bulk, in blends with PS-polybutadiene (SB) diblock copolymer, and also in solution of n-tetradecane (C14) that is a nonsolvent to S blocks. For the I blocks of SI in bulk and SI/SB blends the shape of the ε'' curves that reflects the dielectric relaxation mode distribution is much broader than that for homo-PI chains in bulk. The fact implies that the motion of densely populated I blocks tethered on the rigid S domains is severely retarded by the neighboring tethered chains. In PI/SB/PS blends with (I+B)/S content $\simeq$ 50/50, in which the PI chains are confined in lamellae but not tethered, the mode distribution becomes narrow approaching to that of homo-PI. In SI/PB/PS blends with (I+B)/S $\simeq$ 50/50, in which the I blocks are tethered but rather sparsely distributed, the mode distribution also becomes narrower as ϕ_{SI} is decreased. Addition of C14, which goes only into the I phase, releases thermodynamic constraints on the I blocks, leading to a narrower mode distribution close to but not quite to that of PI/C14 solutions. In SI/C14 as well as in SB/C14 solutions under certain conditions, a peculiar mode emerges, which is probably related to the stability of a regular arrey of S-cores of these diblock copolymer micelles in C14 solution.

INTRODUCTION

In a block copolymer system composed of immiscible components several opposing thermodynamic constraints are

competing to govern the morphology and properties: The
segregation effect that is the tendency of the components
to segregate each other; the osmotic effect that tends to
keep the segment density as uniform as possible in each
phase; and the elastic effect that tends to maximize
conformational entropy of each block chain.   As a result
of such competition, a microphase separated (microdomain)
structure is formed in the system, exerting strong
influences on its physical properties.   An interesting
case is a diblock copolymer composed of immiscible rubbery
and glassy components, in which rubbery blocks are tightly
tethered on rigid glassy domains.   The above mentioned
competition prevails primarily in the rubbery phase.   Thus
it provides an interesting model system for studying
dynamics of the tethered chains.

 However, such a study involves a difficult problem:
For example, through viscoelastic spectroscopy, the
response of the tethered chains is often overwhelmed by
the contribution from the rigid glassy domains ot their
regular array, which is thus not easily separated.[1]
Dielectric spectroscopy, on the other hand, is a powerful
technique especially when applied on a special type of
polymer called type-A that has dipoles all aligned
parallel along the chain contour and exhibits dielectric
relaxation called *dielectric normal mode* process due to
the global motion of the chains.[2,3]   The relaxation
reflects fluctuation or autocorrelation of the end-to-end
vector of an individual chain, placed in any environment:
Regardless of the chains being entangled or unentangled,
tethered or unleashed.

 Using SI diblock copolymers of polystyrene (PS) that
has only parpendicular dipoles and cis-polyisoprene (PI)
that has both parallel and parpendicular dipoles,[3] we
attempted to examine by dielectric spectroscopy the motion
of the I blocks tethered on the rigid S domains and
confined in the I microdomain.[4]

MATERIALS AND METHODS

 Styrene-isoprene (SI) diblock copolymers were prepared
via anionic polymerization: First living PI anions were
prepared with sec-BuLi in n-heptane, which was then
replaced by benzene for further addition of PS blocks to
obtain SI samples.[4]   For comparison, we used homo-PI
samples and also PS-polybutadiene (SB) diblock samples.
PB chains do not possess parallel dipoles, and thus do not
exhibit normal modes.   All these samples were of narrow
molecular weight distribution with M_w/M_n < 1.1. The
samples were coded as SI(L-M), SB(L-M), PI(M), PB(M) and
PS(L) with L and M being M_w in kilo dalton.

 Dielectric measurements were made on SI, SB and PI in
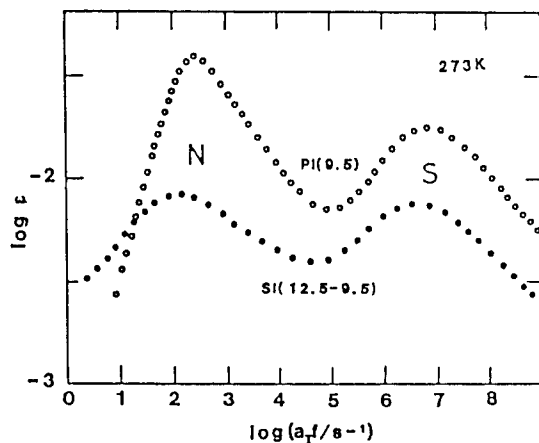bulk and their blends.[4]   In such blends, we often used

Fig.1. ε" master curves reduced to 273 K
of SI(12.5-9.5) and its precursor PI(9.5)
in bulk.

homo-PS and PB to adjust the (I+B)/S volume ratio close to
50/50 to retain an alternating rubbery-glassy lamellar
morphology as much as possible. The measurements were
also made on solutions in a selective solvent,
n-tetradecane (C14) that dissolves only PI and PB and
precipitates PS, and on solutions in a common solvent,
toluene (TL) that dissolves both components equally well.[4]
In the former the interface on which the I or B blocks are
tethered is rigid, but in the latter, it is loose and
easily deformable.
    The dielectric measurements were made with a
transformer bridge (General Radio 1615A) in the range of
frequency f from 20 to 50 kHz and in the temperature range
of 200 to 410 K. For low temperature data of the bulk
films in which S domains are in a rigid glassy state, the
time-temperature superposition was valid with the shift
factor a_T conforming to that of PI or PB in bulk.[4] In the
followings we primarily examine the master curves of
dielectric constant ε' and loss ε" constructed from such
low temperature data.

RESULTS AND DISCUSSION

Bulk systems: Figure 1 compares the ε" master curve of
precusor PI(9.5) with those of SI(12.5-9.5), for which

only low T data have been reduced to 273 K. The high f
loss peaks correspond to the PI segment mode common to SI
and PI, and thus independent of I block molecular weight
M_I. The low f dispersions are, on the other hand,
strongly dependent on M_I, and reflect the normal modes of
I blocks and PI chains. For SI, the low f peak is
considerably broadened and the longest relaxation time τ_n
is prolonged, because of the strong thermodynamic
constraints due to the densely populated surrounding
tethered chains. For SI, the ε'' $\propto$ f dependence is not
seen in the low f limit examined, as opposed to the
precursor PI that exibits the characteristic relaxation
tail where ε'' $\propto$ f.

To see whether the ε'' curve in Figure 1 actually
reflects the motion of a single I block chain in SI as in
the case of pure PI, we examined blends of SI(12.5-9.5)
with SB(8.6-8.5) that has the block length and composition
similar to the SI. Their ε''/C_I vs f/f_{max} curves are shown
in Figure 2 (a) and (c). We also examined blends of
PI(9.5)/PS(10)/SB(8.6-8.5) and SI/PS(4)/PB(2), in all of
which (I+B)/S $\simeq$ 50/50, to see the effects of releasing
tethered I- or B- chains from the SI/SB blends. The
results are shown in Figure 2 (b) and 2(d).

In SI/SB blends, the I+B mixed phase form lamellae, in
which dielectric correlation among I-blocks, if exists,
should have been reduced as SI is replaced by di-
electrically inactive SB. We found that although the ε''
curve shifts its location to high f side with decreasing
SI content ϕ_{SI}, the shape of the ε'' curve that reflects
the distribution of relaxation times remains unchanged
(cf., Fig. 2c). On the contrary, in PI/PS/SB blnends in
which I-chians are released from the rigid S-domain
interface, the shape of the ε'' curves is again the same
but is narrower than that of SI and SI/SB blends, and is
close to that of PI as represented with the Rouse and/or
tube model.

In I+B lamellae of SI/PS/PB blends, tethered I-blocks
are sparsely distributed on the S-interface and free PB
chains released from SB fill the space. These blends are
rather unstable because of the lack of SI (or SB)
stabilizing the microdomains. Thus we could not reduce
ϕ_{SI} much in the blends. Still we see in Figure 2 (d), as
SI is replaced by PS+PB, the ε'' curve shifts to the high f
side and its shape also becomes narrower approaching to
that of PI/PB blends which is the same as that of homo-PI.

The broadening of the ε'' curves of SI and SI/SB blends
is presumably due to large scale synchronized waving
motion of the densely populated tethered I (and B) blocks.
The motion of less densely populated I-blocks in SI/PS/PB
blends is restricted to some extent but much less than
that in SI and SI/SB blends. The free PI chains in
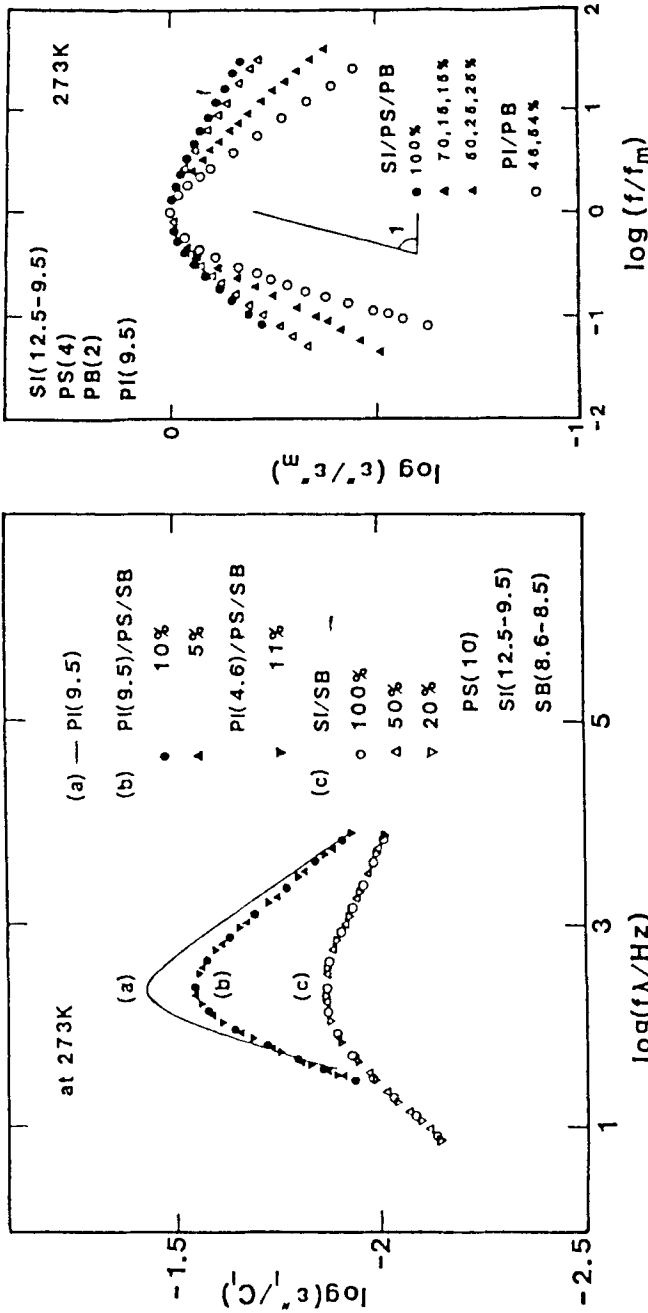PI/PS/SB blends are confined in the narrow I+B lamellae

Fig.2. Comparison of ε'' curves reduced by I content C_I and shifted by $\lambda = f_{max}^{-1}$ for (a) homo-PI; (b) SI/SB blends; and (c) PI/PS/PB blends (left panel); and (d) $\varepsilon''/\varepsilon''_{max}$ vs f/f_{max} curves for SI/PS/PB blends and PI(9.5) (right panel). All data are reduced at 273 K.
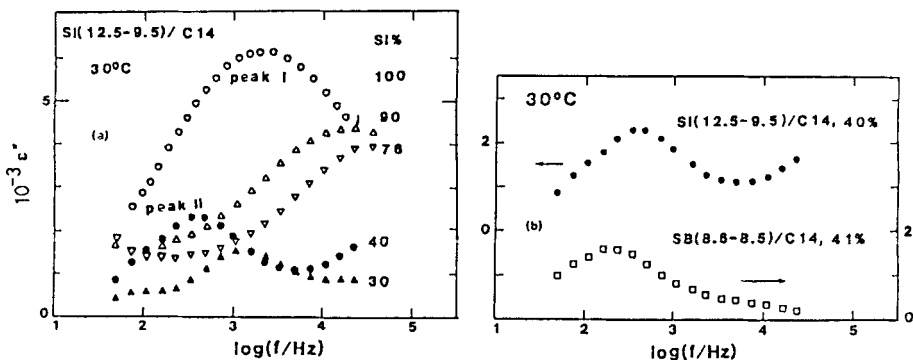
Fig.3. (a) Changes of ε'' curves at 30°C of SI(12.5-9.5)/C14 with ϕ_{SI}; and (b) comparison of ε'' curves at 30°C of SI(12.5-9.5)/C14 and SB(8.6-8.5)/C14 at 40%.

but not tethered on the S-interface, thus their motion is far less severely restricted than the tethered chains but less free than the unrestricted homo-PI chains in bulk and in PI/PB blends.

n-Tetradecane (C14) solutions: When an I-selective solvent, n-tetra- decane (C14) is added to a bulk SI system, the solvent goes almost exclusively into the I phase increasing its volume fraction and reducing the I segment concentration in the I (+C14) phase, but the S domains still remain rigid. We then expect that although the I blocks are still tightly tethered, the osmotic and elastic effects, imposed on their motion should have been significantly reduced.

Figure 3 shows the ε'' curves reduced at 30°C of (a) SI(12.5-9.5)/C14 with ϕ_{SI} decreasing from 100% to 30%, and from 100% to 30%, and (b) the SI/C14 and SB(8.6-8.5)/C14 with ϕ_{SI} = 40%. For high ϕ_{SI} ($\leq$ 76%) solutions, the ε'' peaks reflect the normal mode process of the I blocks. However, for low ϕ_{SI} ($\geq$ 40%) solutions, the corresponding normal mode peaks (peak I) are not seen but a new peak (peak II) emerges that is also seen in SB/C14(40%) (cf., Fig. 3b), on which we will discuss later. (The ε'' peaks due to S segments appear in a much higher f range ($\geq$ 10 MHz) inaccessible to our bridges.)

The peak location of the normal modes of SI/C14 shifts to high f side in a rather complicated manner and the shape becomes somewhat sharper with decreasing ϕ_{SI}. For precursor PI/C14, the loss curves shifted their location without changing their shape.
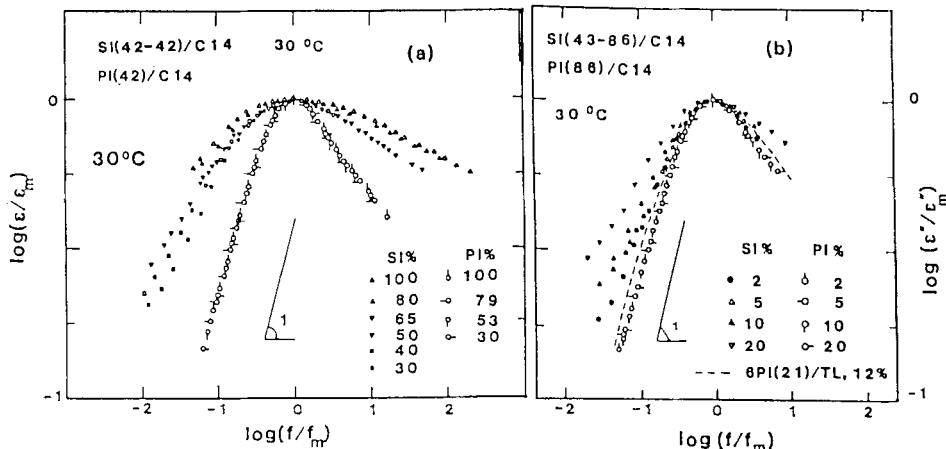
Fig.4. Comparison of reduced ε'' curves at 30°C (a) for SI(42-42)/C14 and PI(42)/C14 with various SI and PI concentrations ϕ_{SI} and ϕ_{PI}; and (b) those for SI(43-86)/C14 and PI(86)/C14 with various ϕ_{SI} and ϕ_{PI}. The dashed curve is for 6-arm star 6PI(21)/TL with ϕ_{PI} = 12%.

   To see the features of the changes in the ε'' curves, we compared in Figure 4(a) the normalized $\varepsilon''/\varepsilon''_{max}$ vs f/f_m curves at 30°C of the same SI(42-42)/C14 against its precursor PI(42)/C14, and (b) those of SI(43-86)/C14 and its PI(86)/C14 with decreasing ϕ_{SI} (or ϕ_{PI}) from 20 down to 2%. With decreasing ϕ_{SI}, the shape of the normalized ε'' curves becomes sharper, and approaches to that of the precursor PI/C14 solutions that is independent of ϕ_{PI}. However, even the ε'' curve of the 2% SI/C14 solution shown in Figure 5(b) is broader than that of 6-arm star PI, 6I(21), C14 solution. These results indicate the addition of C14 reduces significantly the thermodynamic constraints on the tethered I block chains, as anticipated.
   To examine the nature of the new ε'' peaks (peak II) found in both SI(12.5-9.5) and SB(8.6-8.5), we compared in Figure 5 the changes of ε'' curves of their 40% C14 solutions with temperature. With increasing temperature up to 80°C, the peaks II rapidly diminish. Since we see the peaks in both SI and SB solutions, these peaks must be due to the S segments of the block polymers. Our preliminary SAXS and dynamic viscoelastic spectroscopy suggested that SI or SB micelles with S cores still existed at these tempeatures, but the higher order structure of the micelles (the macrolattice) began to
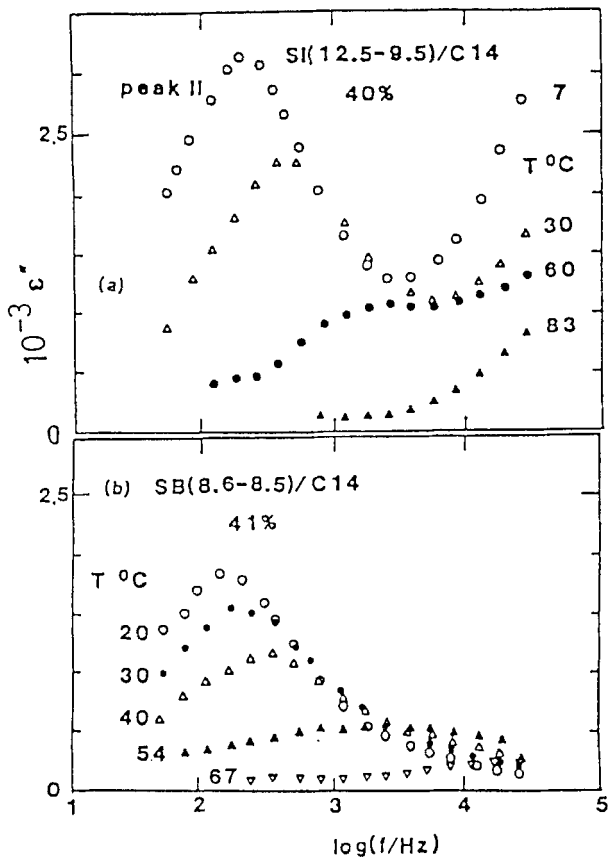
Fig.5. Changes of ε'' curves covering
the peak II area for SI(42-42)/C14 and
SB(41-42)/C14 at 40% with temperature.

become unstable or disordered at the temperature at which
the peak II disappears.[1]

Toluene solutions: By adding a common solvent,
toluene (TL), that goes into both I- (or B-) and S-phases,
we have a system with soft (S+TL) domains and loosely
bound I blocks diluted with TL, or even we have a
hongeneous solution without any phase separation taking
place. Although we do not show the data here, in
SI(42-42)/TL with $\phi_{SI} \leqq 25\%$ the ε'' curves exhibit a single

ε" peak, independent of ϕ_{SI}, while in those with $\phi_{SI} \gtrsim$ 30%, the ε" curves exhibit two peaks. However, in SB(41-42)/TL with any ϕ_{PB}, we do not see any corresponding ε" peaks, the peaks found in SI/TL solutions should be due to the normal modes of the I blocks.

According to SAXS results on SI(42-42)/TL,[5] the solution undergoes microphase separation around $\phi_{SI} \simeq 13.3$ ~ 24.5 at 0°C, which appeared to accompany rather sudden change in the shape of the ε" curves found between 25 and 28%. Unlike in the SI-bulk and SI/C14 solutions, the S phase of the SI/TL solutions is in the rubbery to flow region, the I blocks are not tightly tethered on the interface but their junctions are readily mobile. This situation is reflected in the double peaks of microphase separated SI/TL solutions. On the other hand, the behavior of homogeneous single phase SI/TL systems can be described quite well by an earlier theory of Stockmayer-Kennedy[6] dealing with a Rouse chain composed of two blocks with different local friction coefficients.[4] These problems will be discussed in later publications in greater detail.

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