Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


Supporting Information

# Prediction of Glass Transition Temperature and Design of Phase Diagrams of Butadiene Rubber and Styrene Butadiene Rubber via Molecular Dynamics Simulations

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Table S1 Isomeric contents dependent of $T_g$ of BR by Eqn (1)

| **Weight fraction of BR** | | | **$T_g$ (°C)** | |
|---|---|---|---|---|
| **c-BR** | **t-BR** | **v-BR** | **simulation[a]** | **experiment[b]** |
| 0.976 | 0.02 | 0.005 | -109.4 | -111 |
| 0.975 | 0.025 | 0.005 | -109.7 | -109 |
| 0.97 | 0.026 | 0.005 | -109.3 | -108 |
| 0.987 | 0.07 | 0.006 | -115.5 | -111 |
| 0.979 | 0.014 | 0.007 | -109.1 | -112 |
| 0.964 | 0.029 | 0.007 | -108.9 | -111 |
| 0.978 | 0.015 | 0.007 | -109.1 | -108 |
| 0.978 | 0.014 | 0.008 | -109.0 | -108 |
| 0.959 | 0.033 | 0.008 | -108.8 | -104 |
| 0.859 | 0.133 | 0.008 | -107.6 | -110 |
| 0.911 | 0.079 | 0.01 | -108.0 | -105 |
| 0.954 | 0.035 | 0.011 | -108.5 | -108 |
| 0.975 | 0.012 | 0.013 | -108.5 | -110 |
| 0.954 | 0.031 | 0.015 | -108.1 | -109 |
| 0.951 | 0.034 | 0.015 | -108.1 | -105 |
| 0.951 | 0.028 | 0.021 | -107.5 | -108 |
| 0.914 | 0.052 | 0.034 | -105.9 | -108 |
| 0.927 | 0.036 | 0.037 | -105.8 | -107 |
| 0.925 | 0.037 | 0.038 | -105.7 | -108 |
| 0.894 | 0.068 | 0.038 | -105.3 | -109 |
| 0.919 | 0.042 | 0.039 | -105.5 | -109 |
| 0.918 | 0.042 | 0.04 | -105.4 | -107 |
| 0.908 | 0.05 | 0.042 | -105.1 | -109 |
| 0.894 | 0.045 | 0.061 | -103.2 | -107 |
| 0.392 | 0.502 | 0.106 | -93.2 | -96 |
| 0.372 | 0.516 | 0.112 | -92.4 | -96 |
| 0.358 | 0.528 | 0.114 | -92.0 | -96 |
| 0.364 | 0.521 | 0.115 | -92.0 | -96 |
| 0.376 | 0.508 | 0.116 | -92.1 | -94 |
| 0.384 | 0.498 | 0.118 | -92.0 | -95 |
| 0.347 | 0.52 | 0.133 | -90.2 | -95 |
| 0.361 | 0.497 | 0.142 | -89.6 | -95 |
| 0.358 | 0.469 | 0.173 | -86.7 | -92 |
| 0.327 | 0.496 | 0.177 | -86.0 | -90 |
| 0.287 | 0.486 | 0.227 | -81.0 | -88 |
| 0.261 | 0.401 | 0.338 | -70.7 | -73 |
| 0.237 | 0.388 | 0.375 | -67.1 | -73 |
| 0.154 | 0.22 | 0.626 | -43.5 | -51 |
| 0.162 | 0.158 | 0.68 | -38.7 | -45 |
| 0.15 | 0.148 | 0.702 | -36.6 | -42 |
| 0.107 | 0.103 | 0.79 | -28.2 | -28 |

[a]Calculated $T_g$ by eqn (1) . [b]Experimental data of $T_g$[66].

Table S2 Isomeric contents dependent of $T_g$ of SBR by Eqn (5)

| **Weight fraction of SBR** | | | | **$T_g$ (°C)** | |
|---|---|---|---|---|---|
| **c-BR** | **t-BR** | **v-BR** | **Styrene** | **simulation[a]** | **experiment[b]** |
| 0.1205 | 0.1205 | 0.654 | 0.105 | -27.31 | -30.01 |
| 0.1185 | 0.1185 | 0.609 | 0.154 | -25.16 | -24.26 |
| 0.111 | 0.111 | 0.575 | 0.203 | -21.94 | -18.27 |
| 0.1035 | 0.1035 | 0.539 | 0.254 | -18.64 | -14.42 |
| 0.3125 | 0.3125 | 0.14 | 0.235 | -60.87 | -62 |
| 0.355 | 0.355 | 0.11 | 0.18 | -70.80 | -70 |
| 0.11 | 0.11 | 0.58 | 0.2 | -21.85 | -33 |
| 0.1 | 0.1 | 0.6 | 0.2 | -19.87 | -34 |
| 0.335 | 0.335 | 0.28 | 0.05 | -70.74 | -77 |
| 0.34 | 0.34 | 0.14 | 0.18 | -67.85 | -70 |
| 0.122 | 0.122 | 0.5 | 0.256 | -22.27 | -20 |
| 0.267 | 0.396 | 0.099 | 0.238 | -63.38 | -66 |
| 0.2775 | 0.2775 | 0.21 | 0.235 | -53.91 | -49.3 |
| 0.125 | 0.125 | 0.5 | 0.25 | -23.07 | -28.9 |

[a]Calculated $T_g$ by eqn (5) . [b]Experimental data of $T_g$[76-80].

**Theoretical Details of How to calculate the mixing parameter of butadiene isomers**

To calculate the mixing parameter and energy that attributes to the $T_g$ of rubber blends, we constructed a model system with one central solute molecule surrounded by the other solvent molecules. We sequentially calculated the mixing energy, the interaction energy, by increasing the number of surrounding solvent molecules. By using mixing energy, mixing parameter, χ, can be estimated from the followed equation:

$$\Delta G_{mix} = RTn_1\emptyset_2\chi_{12} \quad (1)$$

The right-hand side of the number of moles $n_1$, and volume fraction $\emptyset_2$ of solvent polymer. $R$ is the gas constant and $T$ is the absolute temperature.

The mixing parameter of butadiene isomer is very small compared with large mixing parameter of butadiene – styrene. Therefore, butadiene isomers can be easily mixed. It is not the case of the butadiene – styrene. The butadiene isomers show no significant correlation with each other because of the low mixing energy. As a result, the $T_g$ of BR-blends can be easily estimated as described in the eqn (1) of the main text.

Presumably, the high mixing energy and mixing parameter between BR and styrene is responsible for the separated $T_g$ regions predicted in Figure 7.

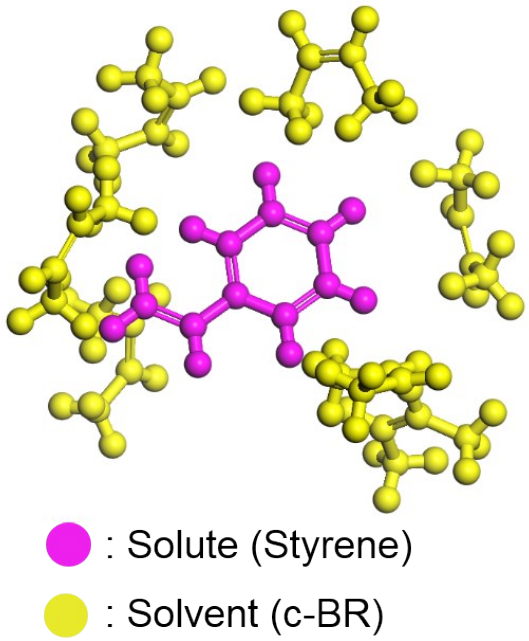


Fig. S1. Example of a rubber blend system (solute: Styrene, solvent: cis-butadiene)

Table S3 Mixing parameter and mixing energy of copolymers

| **Polymer** | **χ** | **$\Delta G_{mix}$ [kcal/mol]** |
|---|---|---|
| cis-BR – trans-BR | 0.034 | 0.020 |
| cis-BR – vinyl-BR | 0.057 | 0.034 |
| trans-BR – vinyl-BR | 0.045 | 0.027 |
| cis-BR – Styrene | 0.475 | 0.281 |
| trans-BR – Styrene | 0.637 | 0.377 |
| vinyl-BR – Styrene | 0.728 | 0.431 |