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Diffusion in Strongly Segregated Block Copolymers

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In a strongly segregated block copolymer system self-diffusion, and other related relaxation and equilibration processes, can only occur by movement of blocks of a single molecule from one microdomain to another. The key element in developing an understanding of these activated kinetic processes is finding the most efficient, i.e., lowest free energy, pathway by which a block can pass through the opposite type domain. Diffusion in block copolymers has been the subject of a number of recent reports.[1-3]

For an A block to pass as a random coil through the B domain would involve an activation free energy $F_c^{\ddagger} = O(f\chi N)$ (see glossary for definitions). In this paper we show that the activation free energy can be reduced to $F_s^{\ddagger} = O[(1-f)(\chi N)^{2/3}]$ (the subscripts c and s stand for coiled and stretched, respectively). This activation free energy is achieved by highly stretching only a part of the A block across the B domain. The stretched part may then enter the new A domain, pulling behind it successive, stretched sections of A block, until the entire transfer has been effected.

We limit our consideration here to the transverse self-diffusion of molecules across a lamellar microdomain structure. Figure 1 illustrates schematically the transfer process leading to $F_2^{\ddagger}$. The tip of an A block moves from a typical position somewhere in the starting A domain (Figure 1a) to the interface of that domain (Figure 1b). It penetrates, and then crosses, the B domain with N_s units of the A block hyperstretched behind it (Figure 1c). (By hyperstretched we mean stretched to a much greater extent than the usual stretching of a block under strong segregation conditions.) The tip can then enter the new A domain, while new sections of the A block, of size N_s, follow behind through domain B (Figure 1d), until the entire A block has left its old domain (Figure 1e). Finally the whole transfer is completed, and the joint moves, along with the B block, to a position in the new domain interphase (Figure 1f). The transfer process is equally likely to occur in the opposite order. Starting from a typical state (Figure 1f) the joint moves across from the interface of one domain to another, together with block B and a hyperstretched section of block A (Figure 1e). The remainder of the A block is then pulled through (Figure 1c,d), and finally the end of the A block assumes a typical position in its new domain (Figure 1a,b).

Our task is to determine the optimal number, N_s, of monomers in the stretched A segment that spans the hostile territory. A Flory-type argument, such as was used to derive the stretching caused by excluded volume, not only yields order of magnitude estimates but is quantitatively correct to leading order. The activation free energy, $F_s^{\ddagger}$, of the process described above is (throughout this paper all energies will be given in units of k_BT)

$$F_s^{\ddagger} = \chi N_s + \frac{3}{2}\frac{1}{N_s}\frac{{d_B}^2}{b^2} \tag{1}$$

The first term is the energy of the N_s units of A in the B domain. The second is the stretching free energy of these units to span the distance, d_B. Minimizing with respect to N_s yields

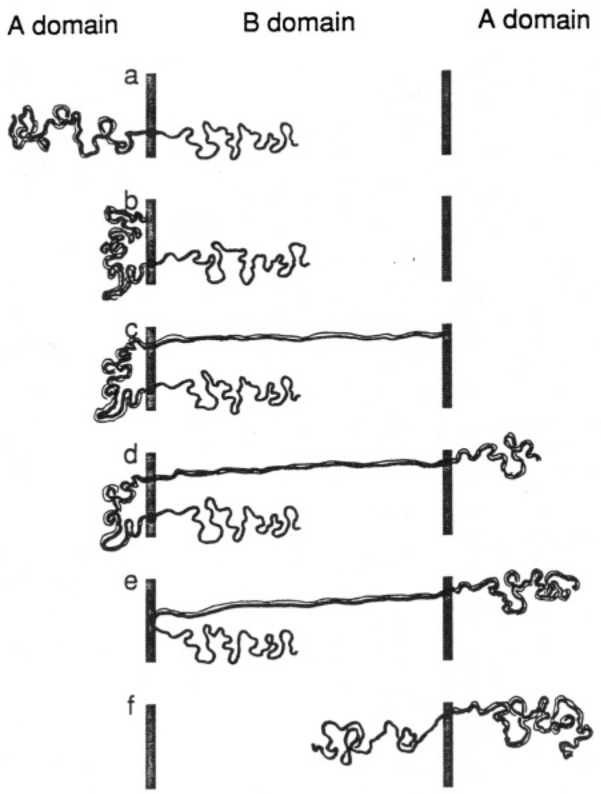

Figure 1. Schematic drawings of stages in the diffusion of a block copolymer molecule across one domain.

$$N_s = \left(\frac{3}{2}\right)^{1/2}\frac{1}{\chi^{1/2}}\frac{d_B}{b} \tag{2}$$

and an activation energy of

$$F_s^{\ddagger} = 6^{1/2}\chi^{1/2}(d_B/b) \tag{3}$$

According to Semenov's[4,5] classical trajectory evaluation of the functional integral arising in block copolymer theory,[6] in the limit of large N the thickness d_B is given by

$$\frac{d_B}{b} = \frac{4}{24^{1/6}\pi^{2/3}}(1-f)\chi^{1/6}N^{2/3} \tag{4}$$

so that the activation free energy is

$$F_s^{\ddagger} = \frac{4(3)^{1/3}}{\pi^{2/3}}(1-f)(\chi N)^{2/3} = 2.69(1-f)(\chi N)^{2/3} \tag{5}$$

Following the transfer of the A block across the B domain, the B block must be transferred across the A domain, with activation free energy

$$F_s^{\ddagger} = \frac{4(3)^{1/3}}{\pi^{2/3}}f(\chi N)^{2/3} \tag{6}$$

The significant activation free energy will be the larger of eqs 5 and 6.

With this result we can see why it was appropriate to use the free space stretching entropy in eq 1. The field acting on a molecule to keep the concentration within a domain uniform[6] is only on the order of the domain free energy per molecule,[4] namely, $O[(\chi N)^{1/3}]$, whereas the stretching entropy of eq 1 is $O[(\chi N)^{2/3}]$.

We must inquire as to which of the activation free energies, $F_s^{\ddagger}$ or $F_c^{\ddagger}$, is smaller, in order to predict the

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dominant mechanism. According to eqs 5 and 6, the stretched chain mechanism will have the smaller activation free energy if $\chi N > 19.45$. This inequality generally has bo be true to be in the strong segregation regime. One has to keep in mind, though, that the estimate lacks some self-consistency, since the asymptotic estimates used by Semenov and in this paper are not strictly valid for such a low value of χN.[5]

It is well to keep in mind how high the activation free energy is. Assume even a fairly low value of $\chi N = 30$, and let $f = 1/2$. Then the activation free energy (over k_BT) is 13.0, or $\exp(-F_s^{\ddagger}) = 2.3 \times 10^{-6}$. Diffusion across the lamellae is a very slow process in strongly segregated block copolymers.

As far as estimating the activation free energy is concerned, it does not matter whether the motion of the diffusing molecule is by reptation or unentangled. With reptation all moves are made by leading with one end of the molecule. In particular this means that in order to follow the tube the B block may have to enter into the A domain, a short section at a time, once the whole A block has left the old A domain. Also in going from Figure 1e to Figure 1d in the reverse mechanism, the B block's end must first traverse the B domain, and then the joint may follow, carrying with it a stretched section of A block. In the case of no entanglements, the joint, or any section of the B block, may go first.

Similar arguments to those of the present letter may be applicable in the calculation of the diffusion rate in all but the weakest of weakly segregated block copolymers,[2] i.e., when there is activation free energy that is not negligible. The arguments are much more detailed, however, so we leave them for a subsequent work.

Glossary

k_BT	Boltzmann's constant times temperature
b	statistical length of a monomer (assumed to be the same for species A and B)
ρ_0	number density of monomers in the pure polymers (assumed to be the same for species A and B)
χ	Flory interaction parameter
K	index indicating either species A or B
$f_A \equiv f$	fraction of A
$f_B = 1 - f$	fraction of B
N	degree of polymerization of the block copolymer molecules
$N_K = f_KN$	degree of polymerization of the K block
d_K	thickness of the K domain (herein assumed to be lamellar)
N_s	number of monomer units stretched across the opposite species' domain during the transition process
$F_s^{\ddagger}$	free energy of activation for the stretched mechanism (divided by k_BT)
$F_c^{\ddagger}$	free energy of activation for the coiled mechanism (divided by k_BT)

References and Notes

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