Simulations of Microphase Separation in Crosslinked Polymer Blends

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SUMMARY: We investigate using bond-fluctuation simulations the behavior of crosslinked symmetric binary A-B polymer blends. The variation of the A-B-interaction parameter leads to microphase separation. We study it by focussing on the structure factor which we determine for different crosslink densities and for different values of the A-B-interaction parameter. The structure factor peaks at smaller values of the scattering vector q than predicted by de Gennes. This finding is in line with recent experiments, which, however, could not clarify its origin. We relate the finding to the topological disorder inherent in the network structure, which allows for large deformations during the separation process.

Introduction

Analytic calculations of randomly crosslinked polymer blends or interpenetrating networks are extremely difficult because of the inherent frozen randomness and of the underlying competing interactions. Different from simple melts, the crosslinks prevent a large scale demixing of the A- and B- chains; this results in microphase separation, i.e. in the presence of rather small A- and B-rich regions. In scattering experiments this determines the appearance of a peak in the structure factor at a non-vanishing wave number q_{max}. This value is related to the mean extension of the microphase patterns. An attempt to quantify demixing goes back to de Gennes who used the similarity of the problem to the polarization of a dielectric medium[1)]. Based on a simple homogeneous network model the predicted characteristic length scale of the separation is of the order of the radius of gyration of the networks strands (parts of the precursor chains between two cross-links). On the other hand, experiments have shown the appearance of larger scales[2)]. However, experimentally demixing goes on both before and during crosslinking, and one can hardly crosslink in a stochastically homogeneous state. The thrust of Ref.1 was to analyse in how far an imposed network hinders demixing, by which the microscopic structure gets in thermodynamic equilibrium with the network. Here simulations

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are in a privileged position, since numerically the A-B interactions can be switched off before and during cross-linking.

Crosslinking in Simulations

We use as simulation algorithm the bond fluctuation model (BFM)[3]. The model is well suited to describe the universal properties of dense polymer melts. The case of cross-linking and some properties of the resulting polymer networks were reported in previous work[4-6]. The BFM neglects all chemical details and models polymer chains as sequences of cubes (polymer segments) on a cubic lattice. The cubes are linearly connected via a set of 108 possible bond vectors of length 2, $\sqrt{5}$, $\sqrt{6}$, 3 and $\sqrt{10}$. This restriction of the bonds, together with the requirement that no lattice site can be doubly occupied, leads automatically to the non-intersection of chains during the simulation. To account for the A-B interactions, we envisage an interaction sphere around each cube; the sphere consists of 24 lattice sites (see Fig.1 in Ref.7). For each of such site occupied by a segment of the other species the interaction energy is counted to be E_{AB} (in units of k_BT). This leads to an average interaction energy per A-B-pair of $E=2.02\ E_{AB}$[7]. Note that E is directly proportional to the Flory-Huggins parameter χ, where the effective coordination number p_{eff} is the proportionality factor.

Since former simulations indicated large scale inhomogeneities in the crosslink topology we chose here a very large simulation box, consisting of 400 × 400 × 400 lattice sites. We created in this volume 40000 chains of length 100, fact leading to a lattice occupation density of 0.5 (which corresponds to a dense melt in the framework of the BFM).

The equilibrated melt was then crosslinked randomly by adding bonds, at $E_{AB}=0$, until a preset crosslink density P_{net} was reached (P_{net} denotes the probability that a given segment is part of a crosslink). During crosslinking we made no distinction between the A- and B-segments (cubes). In this way for $P_{net}=0.07$ only 0.6% of the chains do not belong to the network (unconnected or only connected to themselves). In different realizations of the network we also varied the value of P_{net}.

Results

After crosslinking we increased stepwise, as a function of time, the interaction parameter E_{AB}. Fig.1 shows the temporal evolution of N_{AB}, the number of A-B contacts for different values of

P_{net}. Now N_{AB} is related to the internal energy of the system. After each stepwise increase of E_{AB}, N_{AB} decreases first sharply and then exponentially.

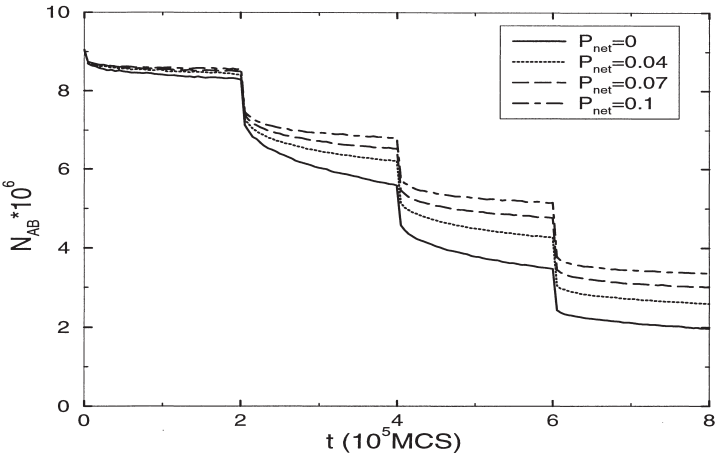

Fig.1: Decrease of N_{AB}, the number of A-B contacts, under changes of the interaction parameter E_{AB}. Here E_{AB} is set to 0.01 at t=0, 0.05 at t=$2*10^5$ Monte Carlo Steps (MCS), 0.1 at t=$4*10^5$ MCS and 0.2 at t=$6*10^5$ MCS.

The separation of the A- and the B-segments is reflected in the A-B-structure factor

$$S(\mathbf{q})=\frac{1}{N}\sum_{n,m} a_n a_m \exp[i\mathbf{q}(\mathbf{R_n}-\mathbf{R_m})], \qquad (1)$$

where a_i equals 1 (-1) when site i is occupied by an A-(B-)segment, and is zero otherwise. We show S(q) for P_{net}=0.07 in Fig.2. In the inset we follow the temporal evolution of S(q) and present it for the times t=$6*10^5$ MCS, t=$8*10^5$ MCS, t=$1*10^6$ MCS and t=$1.2*10^6$ MCS. Here only a single change in E_{AB} occurred, namely at t=$6*10^5$ MCS, from 0.1 to 0.2. The relaxation behavior for a fixed E_{AB} can be described by an exponential decay from the initial value $S_0(q)$ to an extrapolated equilibrium value $S_{eq}(q)$:

$$S(q,t)=S_{eq}(q)+[S_0(q)-S_{eq}(q)]\exp[-t/\tau(q)]. \qquad (2)$$

The upper, dot-dashed line of the inset represents the limiting structure factor $S_{eq}(q)$, obtained by extrapolating S(q,t) using Eq.2.

We observe in every case that $S_{AB}(q)$ has a peak at a nonzero value q_{max}. For samples without crosslinks q_{max} decreases with increasing time; this is due to the growth of the domain sizes. On the other hand, for cross-linked samples q_{max} tends asymptotically to a fixed, nonzero value.

We note that the q_{max}-values obtained by us for the three cross-link densities considered are consistent with a linear dependence of q_{max} on $1/R_{str}$, where R_{str} is the average end-to-end distance of the strands. We find namely from a linear fit:

$$q_{max} \cong \frac{1}{4}\frac{2\pi}{R_{str}}. \qquad (3)$$

This means that the average domain sizes are roughly four times larger than calculated by de Gennes, Eq.(13) of Ref 1.

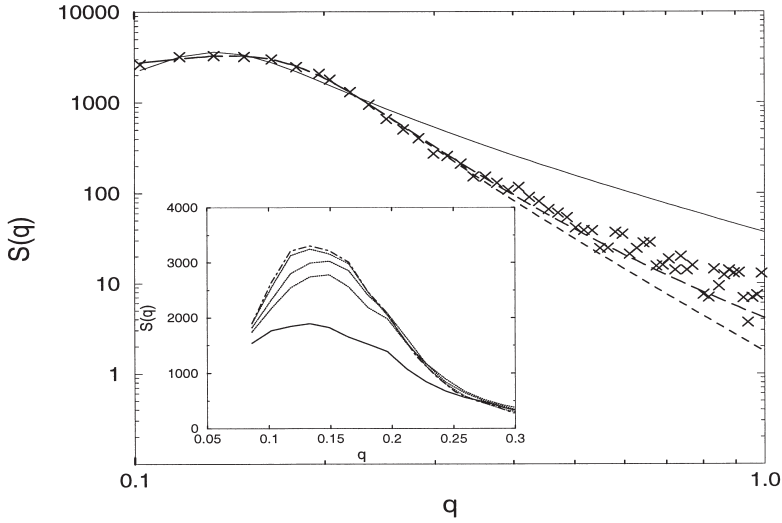

Fig.2: Fits of Eqs.(4) (full line), (5) (long-dashes) and (6) (short dashes) to the structure factor obtained for P_{net}=0.07 and E_{AB}=0.2. Inset: Time development of the structure factor. The dot-dashed line shows the extrapolated values.

The full line in Fig.2 is the fit of our S(q) with the expression put forward by de Gennes in Ref.1:

$$S(q)^{-1}=Aq^2+B+C/q^2. \qquad (4)$$

This expression implies at intermediate q that $S(q) \propto q^{-2}$, whereas we find rather that $S(q) \propto q^{-x}$ with x being near 4. Benmouna et al.[8] generalized the approach of de Gennes by also including screening. They find:

$$S(q)^{-1}=Aq^2+B+C/(q^2+\kappa^2). \quad (5)$$

The fit of our data by this function is also shown in Fig.2, namely through a long-dashed line. Furthermore Alig et. al.[8] considered the simultaneous crosslinking and spinodal demixing of polymer blends. Their expression for S(q) is basically:

$$S(q)^{-1}=q^2(Aq^2+B+C/q^2), \quad (6)$$

and the corresponding fit in Fig.2 is given as a short-dashed line. Clearly, both Eqs. (5) and (6) reproduce our data well, much better than Eq. (4).

We relate our observation that the segregated patterns show dimensions larger than the average strand length to the local structural properties of the network. For this we have also investigated the mobility of the individual segments. Fig.3 shows for P_{net}=0.07 and the same

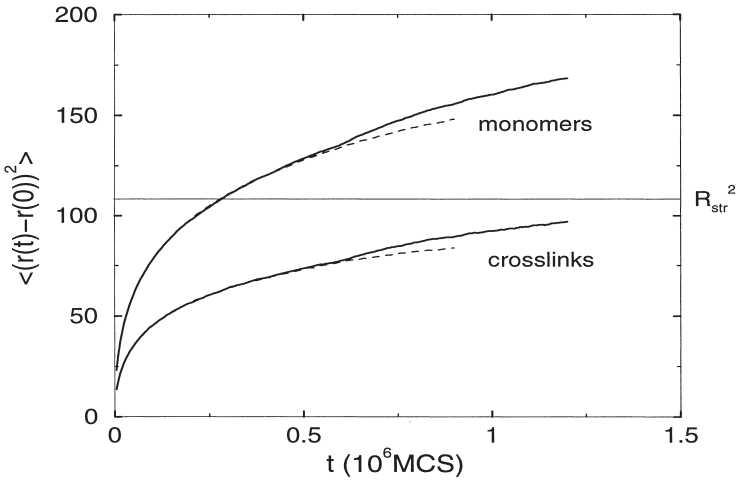

Fig.3: Shown is for P_{net}=0.07 and for $E_{AB}(t)$ as given below Fig.1 the mean square displacement of all monomers and of those involved in crosslinks. The full lines represent the situation of the A-B blend, the dashed lines that of a homopolymer network. The horizontal line indicates the average quadratic strand length.

$E_{AB}(t)$ as above the mean square displacement during separation, first, of all monomers (upper line), and second, of the monomers involved in crosslinks (lower line). The dotted lines show as comparison the mean square displacement in the absence of A-B interactions. We infer that even in the crosslinked system the segment mobility is very high, fact due to the possibility of large scale rearrangements.

Conclusion

Here we have shown that crosslinked A-B polymer blends display under the subsequent inclusion of segment-segment repulsions the appearance of microregions of dimensions much larger than the average length of the net strands. Furthermore the A-B-structure factor shows pronounced deviations from the q^{-2}-behaviour suggested by de Gennes, and the mean squared displacement of the segments as a function of time is quite large. We attribute these effects to the large scale heterogeneities which are present even in interaction-free stochastically crosslinked networks.

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