Structure–Property Correlation of Polymers, a Monte Carlo Approach

Wolfgang Paul* and **Kurt Binder**

Institut für Physik, Johannes-Gutenberg-Universität Mainz, Postfach 3980, D-6500 Mainz, Federal Republic of Germany

Kurt Kremer

Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-5170 Jülich, Federal Republic of Germany

Dieter W. Heermann

Institut für Theoretische Physik, Universität Heidelberg, Philosophenweg 19, 6900 Heidelberg, Federal Republic of Germany

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ABSTRACT: A new approach to deduce macroscopic properties of specific polymer melts using Monte Carlo coarse graining is proposed. Distribution functions for bond lengths and angles of chemically realistic single chains are used as input. As a first application we predict the Vogel–Fulcher temperature for Bisphenol A polycarbonate.

The chemistry of polymers produces an increasing amount of different new species with a wide variety of physical properties such as entanglement length or glass transition temperature. There exist several attempts, where one tries to estimate properties from microscopic modeling. One class of attempts originates in quantum chemistry, where properties are estimated as a sum of contributions of a single constituent of the given monomer.[1] This approach must fail as soon as configurational interactions come into play. The other more sophisticated approach uses a detailed model of the chains and analyzes frozen systems.[2] There, however, only information about statics of a quenched state at temperature $T = 0$ K is available. Quantities like the aforementioned ones thus cannot be understood by such methods. The challenging problem however is to correlate the local chemical structure with the macroscopic properties.[3] For the different modifications of polycarbonate (PC) for instance, rather weak modifications of the local chemical structure cause huge variations in the glass transition temperature T_G or the entanglement molecular mass M_e.[4] In general M_e varies for more than an order of magnitude for the various polymers investigated up to now.[5]

It is the aim of the present article, to report a first attempt to relate configurational averages to a macroscopic observable quantity, namely the Vogel–Fulcher temperature T_0, which is directly related to the glass transition temperature. To do this we take Bisphenol A polycarbonate (BPA–PC) (see Figure 1), because of above mentioned aspects. A first brute force approach would be to simulate BPA–PC with a variety of proposed force fields by a standard molecular dynamics technique. However, this approach is not feasible at all, even for supercomputers of the next few generations.[6] All computer time is used to integrate out the fast irrelevant degrees of freedom. Here we take the opposite approach. The idea is to modify the parameters of a simple lattice polymer model only as much as absolutely necessary in order to account for the essential properties of a given species. As the computational basis we take the 3d version of the bond fluctuation model.[7] In this model the monomers occupy a cube of eight lattice sites, while the bond length varies between 2 and $10^{1/2}$ on a simple cubic lattice. The excluded volume constraint is trivially taken into account by only allowing single occupancy of the lattice sites. This combines the advantages of continuum models with the very fast lattice algorithms. A rather detailed previous study of the static and dynamic properties of dense solutions and melts, using this algorithm,[8] provides us with the necessary basic information about the model. There the qualitative properties of polymer melts are well reproduced.

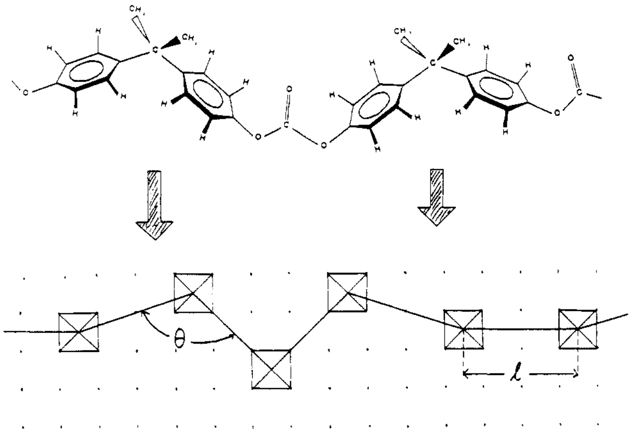

Figure 1. Illustration of the mapping procedure for BPA–PC onto the monomers of the lattice model.

Our aim is to deduce properties of PC melts from the model by mapping configurations. We do not attempt a one-to-one mapping between monomers. While for polymers like polyethylene (PE) one model monomer corresponds to several PE monomers, the situation for PC is just the opposite, because of the large size of the PC monomer. The procedure follows three main steps. First the density of PC gives the length scaling for a given density of chains on the lattice. This also determines the monomer

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ratio. Secondly we use a simple RIS (rotational isomeric state) model[10] to generate bond length and bond angle distributions for an effective chain. This effective chain connects the mass centers of adjacent groups of the chosen PC repeat units. Via a potential in the bond fluctuation model these distributions are reproduced. In the final step we then simulate a melt of model chains with the before determined short-range intrachain potential plus the self and mutual avoidance condition. The temperature can be varied by a suitable Boltzmann factor in the Metropolis sampling.[9]

PC has a density $\rho_{PC} = 1.05$ g/cm^3 ($T = 570$ K) and a monomeric mass $M_{PC} = 425 \times 10^{-24}$ g. In order to obtain the same effective density, we have to map the number densities ρ_{PC}/M_{PC} and $\phi/8$, where ϕ is the volume fraction on the lattice (note that each monomer occupies 8 lattice sites). We represent m PC monomers by n model monomers. With l being the lattice constant this requires

$$n\phi(l/s)^3/8 = m\rho_{PC}/M_{PC} \tag{1}$$

giving

$$s = \left(\frac{\phi n M_{PC}}{8 m \rho_{PC}}\right)^{1/3} / l \tag{2}$$

with s being the length scaling, in angstroms. In general this allows for a huge variation in length scaling and mapping. However the physically reasonable parameter region is rather constrained. The simulations should run at melt densities, which in our case is $\phi = 0.5$.[8] In addition, the fluctuation in the lattice model is rather constraint and should be compared to a chemical unit, which gives a rather smooth distribution of angles and bond lengths. In the present example we chose $m = 1$ and $n = 3$. The mapping of three model monomers onto one PC monomer allows us to properly take into account the intrinsic flexibility of the PC units. From the RIS simulation (at $T_{ref} = 570$ K),[10] where the six intrinsic torsional degrees of freedom are used, we get an average bond length $l_{PC} = 10.16$ Å with a squared variation $\delta l^2 = 2.55$ Å^2. The bond length is taken as the distance between the centers of gravity of two consecutive monomers. The angle θ between two such bonds is $\theta_{PC} = 118°$ with a squared variation of 776. This is to be compared to the lattice model. We generate nonreversal random walks with a bond potential $U(l)/k_BT_{ref} = a(l - l_0)^2$ and an angular contribution $V(\theta)/k_BT_{ref} = b(\cos\theta - \cos\theta_0)^2$, a, l_0, b, and θ_0 being fit parameters. By using the length scaling of eq 2 these parameters are optimized to fit the distributions for PC and for computational efficiency. For $T_{ref} = 570$ K we get $a = 4.0$, $b = 5.0$, $\theta_0 = 90°$, and $l_0 = 3.0$, while one lattice constant corresponds to 2.03 Å. So far we determined the short-range intrachain properties. The distributions of lengths and angles define probabilities portional to $\exp(V(\theta)/kT)$ and $\exp(U(l)/kT)$. A melt of such chains now is simulated at a density of $\phi = 0.5$. The long-range intra- and interchain interactions are taken into account only via the excluded volume condition. Whenever complicated interactions between nonbonded monomers, which go beyond the simple excluded volume constraint, are screened on a length scale comparable to the coarse graining length, the present simplifications should be feasable. There is no principal restriction to modify the model and make it more complicated. One could of course supplement the model by including, e.g., dipole moments of the lattice monomers, if one, in detail, understands the microscopic interactions of the polymer melt under consideration. Our aim however is to modify the simple coarse grained model only as much as absolutely necessary. Thus the present approach should be a rather general starting point. We ran 33 systems of 200 chains. Each chain contained 20 monomers, roughly corresponding to PC oligomers of about 7 monomers or a molecular weight of about $M = 1700$. The temperature was varied by employing the ratio of the corresponding Boltzmann factors for the Metropolis sampling. By this we studied the statics and the dynamics of such a polymer melt as a function of the temperature. The strengths of the fitted effective model potentials set the temperature scale for local relaxations of the model chain. For the present choice of parameters this is close to the typical barrier height of BPA-PC. The static properties of the simulated chains are consistent with experiment. Here we only discuss the diffusion constant. One does not have an absolute time scale from such a simulation; however, the ratio of the diffusion constants should well compare to the experimental systems, if our ansatz incorporates the essential physics. Figure 2 shows a Vogel–Fulcher plot of the diffusion constants. The data extrapolate to the Vogel–Fulcher temperature $T_0 = 250$ K. The exitation barrier $A = 1726k$, in excellent agreement to the experimental value.[11] T_0 turns out to be about 100 K too low. However, since the chains are much shorter than M_e[4] a typical lowering by about 50 K is to be expected. Considering the fact, that we present here a very first and rather simple approach to correlate individual structural properties of a single chain to physical properties of a melt, the results are very promising. Right now we are testing different mapping ratios. In order to test the general validity of this ansatz, we are extending this study to the various modifications of PC as well as other polymer systems. To conclude, we think that this way of reasoning points toward a very interesting future development.

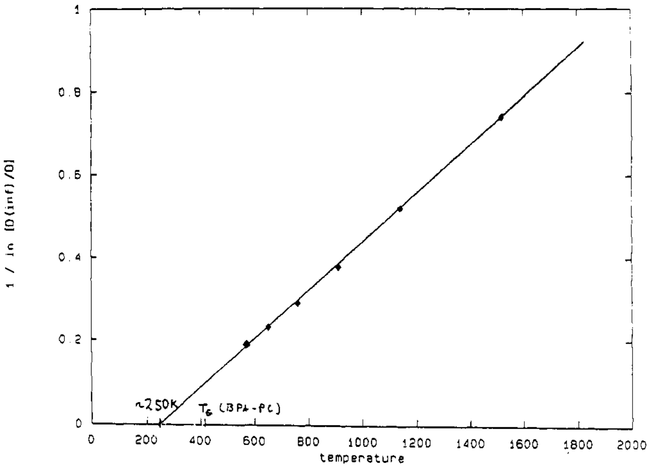

Figure 2. Vogel–Fulcher plot of the relative diffusion constants versus temperature T. The extrapolation toward $D = 0$ gives $T_0 = 250$ K. The normalization D_{inf} corresponds to the simulation without any additional interaction besides the excluded volume constraint.

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Registry No. (BPA)(PC) (SRU), 24936-68-3; (BPA)(PC) (copolymer), 25037-45-0.