Curie Temperature of a Ferromagnetic Polymer Chain Model

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ABSTRACT: Phase transition of a self-avoiding walking polymer chain with spatial nearest neighbor ferromagnetic Ising interaction on the simple cubic lattice is investigated using Metropolis dynamic Monte Carlo technique. Magnetic susceptibility χ is determined from the Brillouin function and from the linear response of magnetization to external magnetic field in small field region. We find the later is better, though both are in consistent with each other at high temperatures. The magnetic susceptibility χ can be expressed using the Curie law and thus the Curie temperature θ is estimated. The chain length dependent Curie temperature θ of the chain model can be well fitted as $\theta = 1.40 - 4.0 \times n^{-0.619}$ based on the finite-size scaling law. The transition temperature for an infinite long chain $\theta(\infty) = 1.40 J/k_B$ and the exponent $\phi = 0.619$ are in agreement with our previous study (J Chem Phys 2003, 119, 2439). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 969–973, 2006

Key words: Curie temperature; phase behavior; magnetic polymers; Monte Carlo simulation

INTRODUCTION

Curie temperature, or Curie point, is the temperature at which a ferromagnetic material being heated loses its ferromagnetism and becomes paramagnetic. An applied magnetic field has a paramagnetic effect on the magnetization of materials. However, below the Curie point, the combination of paramagnetism with ferromagnetism leads to the magnetization following a hysteresis curve with the applied field strength. The Curie temperature is a second-order phase transition and a critical point where the magnetic susceptibility is theoretically infinite.

Magnetic properties of organic materials have been studied for over 150 years and they have received considerable attention since organic ferromagnet poly-BIPO [1,4-bis(2,2,6,6-tetramethyl-4-oxyl)-4-piperidyl-butadiin] was reported in 1987.[1-4] The flexibility, low loss, thin-film-forming ability, and low density will ensure the ferromagnetic polymers play important roles in technology,[5] such as in fields of communication, energy, and information. Most of the ferromagnetic polymers synthesized are coordination polymer composed of transition metals, such as Fe, Co, and Ni,

and various ligands.[6-9] However, the ferromagnetic polymer can also be an organic polymer,[10,11] such as poly-BIPO, *p*-NPNN, or even a carbon-based polymer.[12] A considerable number of mechanisms have been established to explain ferromagnetic interactions among chain's segments. Experiments on magnetic polymer revealed that there exist ferromagnetic spin-couplings and the spin quantum number S can be as big as 5000.[12] For most cases, experimental results can be well explained by Ising or Heisenberg interactions among spins.[8,10,13-15] The existence of a nonzero Curie temperature depends on the interactions as well as on the structure of the materials.

Single chain magnets have been synthesized recently[13,16,17] and the magnetic behavior can be described roughly by one-dimensional (1D) Ising model.[13] They are paramagnetic as classical 1D system with the critical temperature $T_c = 0$. A nonzero T_c was observed if there is a ferromagnetic inter-chain interaction.[10] Theoretically, single chain ferromagnetism is also possible if there is a ferromagnetic interaction between nearby segments and the chain has a three-dimensional (3D) spatial structure.[18,19] Based on a coarse-grained bond fluctuation model, we proposed a ferromagnetic polymer model in good solvents.[19] On the simple cubic lattice, chain's bond length can fluctuate among values 1, $\sqrt{2}$, or $\sqrt{3}$ in the unit of the lattice constant. The interactions among monomers are (1) self-avoiding and (2) spatial nearest neighbor ferromagnetic Ising

interactions. The model chain undergoes a magnetic phase transition as well as a spatial conformational collapse transition at the critical temperature $T_c^0 \sim$ 1.37J/k_B for long chains, here the superscript 0 represents the zero field case. Variable J is the spin–spin coupling constant and k_B is Boltzmann constant. It was also found that both magnetic and spatial conformational properties are dependent on the external field. Different behaviors are found for the chain at temperatures below and above the zero-field critical temperature T_c^0.[20]

In this article, the dependence of the magnetization on external field is investigated based on the coarse-grained bond fluctuation ferromagnetic Ising chain model. The Curie temperature θ is determined based on the field dependence of magnetization. We find the chain length dependent Curie temperature θ can be fitted by $\theta = 1.40 - 4.0 \times n^{-0.619}$ (J/k_B). The results are in agreement with that obtained from magnetization-temperature property at zero field.[19]

Model and simulation method

The 3D Ising chain model on the simple cubic lattice is described by the following Hamiltonian:

$$H = -\sum_{[ij]} J_{ij}\sigma_i\sigma_j - h\sum_i \sigma_i \tag{1}$$

where $\sigma_i = \pm 1$ are the spin variables at monomers of the chain. The symbol h, which adsorbs the external magnetic field B through $h = \mu_B B$, is in unit of energy, where μ_B is the Bohr magneton. The features of the model are reflected in the spin–spin couplings J_{ij}. In this work, we consider spatial nearest neighbor interactions with $J_{ij} = J$ for $[ij]$ nearest neighbor on the lattice and zero otherwise, i.e., the spin–spin interactions exist only between a pair of spins with spatial distance one lattice size. Here we consider the ferromagnetic case and set the coupling constant $J = 1$ for simplification. The excluded volume of the monomer is also taken into account by the requirement that no lattice site can be occupied simultaneously by two or more monomers, which is called self-avoiding. The spin variable in this model has only two values $\sigma_i = \pm 1$, corresponding to the spin quantum number $S = 1/2$.

The polymer chain is comprised of $n + 1$ identical monomers (i.e., n bonds, monomer numbered from 0 to n) consecutively linked with bond length ranging from 1 to $\sqrt{3}$ on the SC lattice. Each monomer occupies one site of the lattice. The bond between successive monomers can be taken from a set of 26 allowed bond vectors obtained from the set {(1,0,0), (1,1,0), (1,1,1)} by symmetry operations of the cubic lattice.

Change of the configuration contains two aspects: one is the change of spatial configuration and another is the update of spins. The change of the spatial configuration starts by choosing a monomer at random and then attempts to move it one lattice spacing in one of the six randomly selected directions: $\pm x$, $\pm y$, and $\pm z$. This trial move will be accepted if the following four conditions are satisfied: (1) self-avoidance is obeyed, (2) the new bond vector still belongs to the allowed bond set, (3) two bonds do not intersect, and (4) the Boltzmann factor $\exp(-\Delta E/k_B T)$ is greater than a random number uniformly distributed in the interval (0,1), where ΔE is the change in energy due to the trial move. To update the spins, we randomly choose a monomer and flip the spin on it by the Metropolis algorithm. The time unit used in the work is MC step (MCS). One MCS includes $n + 1$ monomer trial movement and $n + 1$ trial spin flip.

Simulation starts from an initial random configuration at $h = 0$. Then, we slowly increase the field up to the maximum $h_{max} = 2.0$ with a very small step Δh. For every field h, system is updated for total $500n^2$ MCS and thus 500 independent samples are recorded with a time interval $\Delta t = n^2$ MCS. The final configuration at the previous field is used as the initial configuration for the subsequent field. At last, the simulation results are also averaged over 1000 initial random chain configurations. In the work, the temperature T is in the unit J/k_B, and the field h and energy E are in unit of J.

RESULTS AND DISCUSSIONS

Figures 1(a) and 1(b) show the magnetization-field ($\langle M \rangle$–h) curves at temperatures $T > T_c^0$ where no hysteresis is observed and the chain behaves as a paramagnet.[20] The magnetization M is defined as the average spin per monomer, i.e., $M = \frac{1}{n+1}\sum_i \sigma_i$. Parentheses $\langle \rangle$ represent average over Monte Carlo samples. The magnetization increases nonlinearly and saturates to $\langle M \rangle = 1$ at enough high field as shown in Figure 1(a). At the same temperature, the magnetization increases faster for a longer chain as shown in Figure 1(b). We will show that the Curie temperature θ is of chain length n dependence as discussed below: θ increases with n (see Fig. 6). Therefore, at any finite temperature above θ, the temperature is closer to θ for a long chain than that for a short chain that makes long chain more sensitive to external field. Thus, a long chain has bigger magnetization than a short one at the same temperature. The $\langle M \rangle$–h curve of the Ising chain model can be described by the Brillouin function $B_j(x)$,

$$<M>/M_s = B_j(x) = \frac{2j+1}{2j} \coth\left[\frac{2j+1}{2j}x\right]$$

$$-\frac{1}{2j}\coth\left[\frac{1}{2j}x\right] \tag{2}$$
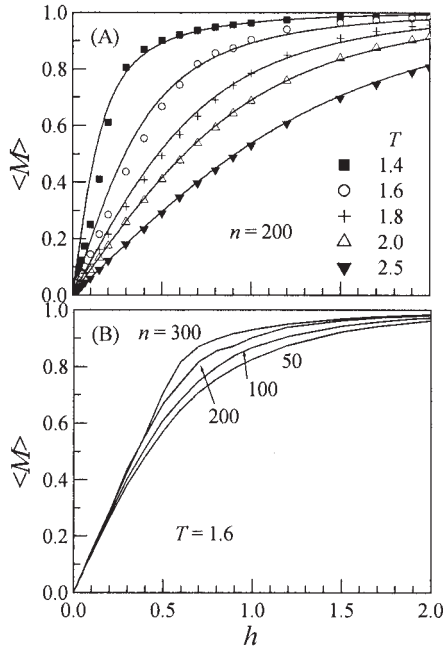
Figure 1 (a) Magnetization-field ($\langle M\rangle$–h) curves at different temperatures $T > T_c^0$ for chain length $n = 200$. The lines are fitting curves of eq. (2). (b) $\langle M\rangle$–h curves for different chain lengths at temperature $T = 1.6$.

with parameter $x = \dfrac{jgh}{k_BT}$. Here, j is the total angular momentum quantum and g the Lande g-factor. For the Ising chain model, the saturation magnetization $M_s = 1$ and the Lande g-factor $g = 2$ (spin system). However, we get value $j > 1/2$, since there exist spin–spin interactions and the value j increases with decreasing the temperature T. Under the external field, spin will align along the field to lower the system's energy. From the point of view of the mean-field theory, the nearest neighbor spins offer an additional magnetic field h' and the spin-field coupling is $(h + h')\sigma_i$ instead of the original coupling $h\sigma_i$. Therefore, we get the total angular momentum quantum j bigger than spin quantum $1/2$. Table I gives some values of j for chain of length $n = 200$. We estimate the value j by best fitting the $\langle M\rangle$–h curve by eq. (2). However, we find the curves get worse with the decrease of the temperature T, especially at weak field region. We find such a situation still exists even if we decrease the field starting from a high field. One possible reason is that both spin configuration and spatial configuration change with the field. As we will show later, the change of spatial configuration accelerates the change process of spin configuration, and at lower temperatures, the process is more profound that makes a deviation from the Brillouin function. In the following, we will show the change of spin and spatial configuration of chain.

Figure 2 gives some typical configurations at different external magnetic fields. At zero field, the chain is

in an extended coil state. The summation of spin $\sum\limits_{i=0}^{n}\sigma_i$ roughly equals to zero. It is clear to see that the spins assemble to form small clusters at the temperature slightly above T_c^0. This observation confirms our previous analysis on the dependence of configurational energy of Ising chain on the temperature,[19] where we find the configurational energy steadily decreases while the magnetization maintains roughly zero at $T > T_c^0$. With the increase of the external field, the chain shrinks and the size of spin cluster increases simultaneously, as shown in Figures 2(b) and 2(c). At high field, a sphere-like chain configuration forms and almost all spins are parallel to the field. Then configuration changes very slowly with field, as that shown in Figures 2(d) and 2(e). For the current chain model, it is clear to see the cooperation of spin and spatial configuration: both change with field and accelerate each other. The phase transition of the Ising chain model is contributed to the cooperation of spin and spatial configuration.[19] We also find the process becomes more profound at low temperatures.

The initial (zero field) magnetic susceptibility $\chi = \dfrac{dM}{dh}$ at very weak fields $h \sim 0$ can be easily derived from eq. (2). At small h or small x, eq. (2) can be expressed approximately as

$$< M > \; = \frac{2(j + 1)}{3T}\, h \qquad (3)$$

using the approximation expression $\coth y = \dfrac{1}{y} + \dfrac{y}{3}$ for small y and setting $\langle M_s\rangle = 1$, $g = 2$, and $k_B = 1$. Therefore, the magnetic susceptibility

$$\chi = \frac{<M>}{h} = \frac{2(j + 1)}{3T} \qquad (4)$$

is derived at weak fields. The calculated χ are presented in Table I. As we point above, however, eq. (2) is difficult to describe the behavior of $\langle M\rangle$–h curve at low temperature. Therefore, the magnetic susceptibil-

TABLE I
Estimated Values of j and Magnetic Susceptibilities χ at Different Temperature for Chain $n = 200$

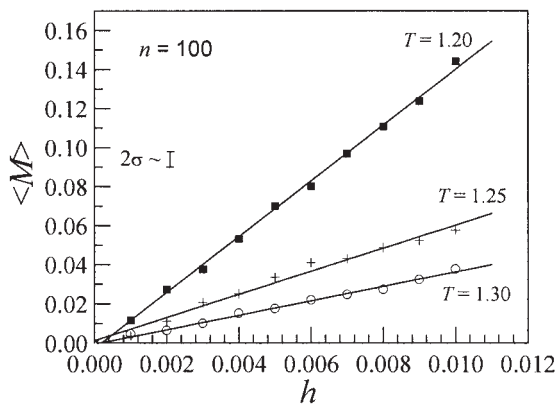| T	j	χ^a	χ^b
1.4	8.8	4.7	2.5
1.6	3.7	2.0	1.5
1.8	2.2	1.2	1.1
2.0	1.7	0.90	0.88
2.5	1.3	0.61	0.61

[a] Estimated from j with eq. (4).
[b] Estimated from linear $\langle M\rangle$-h curve.
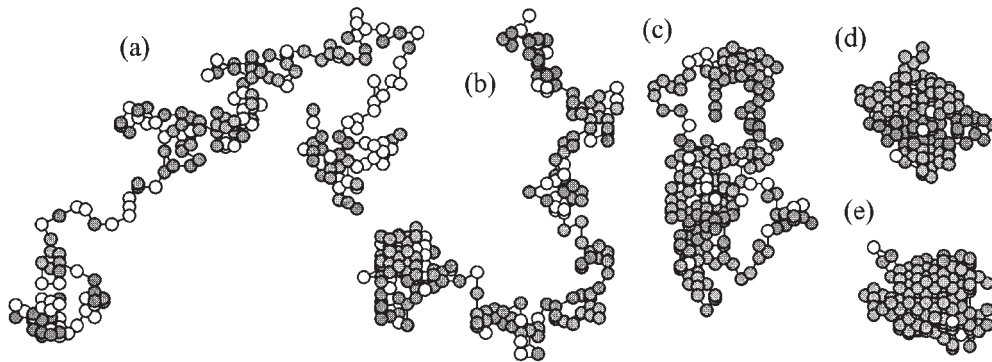
Figure 2 Typical chain configurations at different fields h: (a) $h = 0.0$, (b) $h = 0.4$, (c) $h = 0.6$, (d) $h = 0.8$, and (e) $h = 2.0$. Chain length is $n = 200$ and temperature is $T = 1.6$. Grey circles are spins parallel to the field h, whereas white circles are that antiparallel to the field.

ities χ cannot be precisely estimated by eq. (4). To overcome this difficulty, we have carried out Monte Carlo simulations at very weak fields where the magnetization $\langle M \rangle$ increase almost linearly with field h and the curve roughly passes through zero point. The linear $\langle M \rangle$–h curves for chain length $n = 100$ at different temperatures are shown in Figure 3. The magnetic susceptibilities χ are calculated from the linear fit of the curve near zero field. Figure 4 shows the dependence of the magnetic susceptibility χ on the temperature T for chains $n = 100$ and 200. The magnetic susceptibility of a longer chain is bigger than that of a shorter chain, which is in agreement with that shown in Figure 1(b) where the magnetization increases faster for a longer chain. Some values of magnetic susceptibility χ are listed in Table I for comparing with that obtained from eq. (4). At high temperatures, both give almost the same results, but at low temperatures close to the transition temperature, the magnetic susceptibility χ obtained from linear fit of $\langle M \rangle$–h curve is smaller.

The magnetic susceptibility is nearly zero at high temperature but increases sharply as temperature decreases, indicating a paramagnetic–ferromagnetic transition at low temperature. Above the Curie temperature θ, the magnetic susceptibility can be fitted by the Curie law

$$\chi = \frac{C}{T - \theta} \qquad (5)$$

Therefore, the Curie temperature θ can be easily obtained from the inverse magnetic susceptibility

$$\frac{1}{\chi} = C'(T - \theta) \qquad (6)$$

Figure 5 shows that the magnetic susceptibility of Ising polymer chain can be well fitted by the Curie law. And the coefficient C' in eq. (6), the slope in Figure 5, also increases with the chain length n. The Curie temperature θ is the intercept of the inverse magnetic susceptibility $1/\chi$ with the temperature axis. We find that the Curie temperature θ is of chain length dependence, in consistence with that calculated from

Figure 3 Plots of the magnetization $\langle M \rangle$ as a function of the external field h at very weak fields for chain of length $n = 100$. The standard error 2σ is roughly independent of the field. Straight lines are the linear fitting of simulation data.
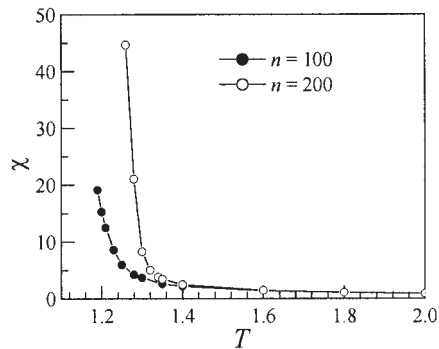

Figure 4 Dependence of the magnetic susceptibility χ on the temperature T.

the temperature dependence of magnetization at zero field.[19]

Since the Curie temperature is a second-order phase transition, then according to the finite-size scaling law,[21] it can be scaled as[22]

$$\theta = \theta(\infty) - an^{-\phi} \qquad (7)$$

with a crossover exponent ϕ. Here $\theta(\infty)$ is the critical temperature of an infinite system, and the Curie temperature θ is that of chain length n. With a least-square fit method and taking account of the error of θ at finite length, we obtain $\theta(\infty) = 1.40 \pm 0.05$ and $\phi = 0.619 \pm 0.005$ for the Ising polymer chain model. In Figure 6, we also plot θ vs. $n^{-\phi}$ using above exponents $\theta(\infty)$ and ϕ. One can see that the critical temperature $\theta(n)$ can be well described by the scaling law. The Curie temperature is in agreement with the estimated critical temperature $T_c^0 = 1.37 \pm 0.05 (J/k_B)$,[19] where the phase transition at zero field was studied. The exponent ϕ is also in agreement with our previous estimation $\phi = 0.633$.[19]

CONCLUSIONS

The response of magnetic polymer chain to external magnetic field is simulated based on a bond-fluctuating SAW chain model with spatial nearest neighbor ferromagnetic Ising interaction on the simple cubic lattice. We find that both the magnetic and spatial conformational properties are dependent on the external field h. The magnetization-field curve above Curie temperature can be described by the Brillouin function with a quantum number j that depends on the temperature. The zero field magnetic susceptibility can be determined from the Brillouin function. It can be also estimated from the linear response of magnetization to external magnetic field in small field region. We find both are in consistent with each other at high temperatures. The Curie temperature can be expressed as
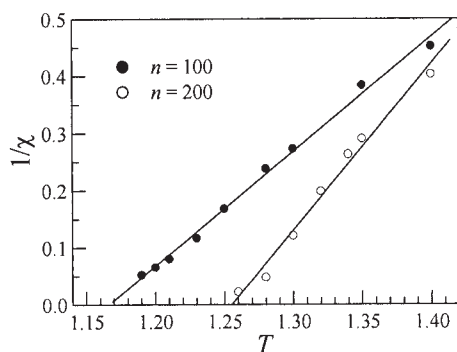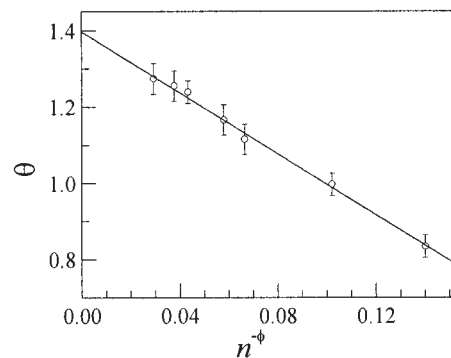
Figure 6 Plot of the Curie temperatures θ vs. $n^{-\phi}$ for chain lengths $n = 20, 40, 80, 100, 160, 200,$ and 300. The straight line $\theta = 1.40 - 4.0\ n^{-0.619}$ is obtained by least-square fitting of the data.

$\theta = \theta(\infty) - an^{-\phi}$ with $\theta(\infty) = 1.40 \pm 0.05$ for infinite chain and exponent $\phi = 0.619 \pm 0.005$. The estimated Curie temperature and the exponent are in consistent with those determined from the temperature dependence magnetization at zero field.

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Figure 5 Plots of the inverse magnetic susceptibility $1/\chi$ as a function of the temperature T. Straight lines are the linear fits according to the Curie law.