Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 45 (2004) 2863–2867

polymer

www.elsevier.com/locate/polymer

Monte Carlo simulation of the response of ferromagnetic polymer chain to external magnetic field

Jian-Hua Huang[a,*], Meng-Bo Luo[b]

[a]Department of Applied Chemistry, Zhejiang Institute of Science and Technology, Wenyi Road 88, Hangzhou 310033, China
[b]Department of Physics, Zhejiang University, Hangzhou 310028, China

Received 16 November 2003; received in revised form 12 February 2004; accepted 13 February 2004

Abstract

The response of ferromagnetic Ising polymer chain in dilute solution to external magnetic field is investigated using Monte Carlo technique. It is found that both magnetic and spatial conformational properties are dependent on the external field, chain length, and temperature. They behave differently at temperatures below and above the zero-field critical temperature T_c^0. Simulation results indicate that the model chain is a possible candidate for recording material and molecular mechanism.

Keywords: Magnetic polymer; Magnetic property; Configuration

1. Introduction

Magnetic properties of organic materials have been studied for over 150 years and they have received considerable attention since organic ferromagnet poly-BIPO was reported in 1987 [1–4]. The flexibility, low loss, thin-film-forming ability, and low density will ensure the ferromagnetic polymers playing important roles in technology [5], such as in fields of communication, energy and information. The magnetic polymer may be an organic polymer [6–8] or a coordination polymer composed of transition metals and various ligands [1,9–11]. Experiments on magnetic polymer usually focused on the magnetic properties of solid state and revealed that there exist ferromagnetic spin-couplings and the spin quantum number S can be as big as 5000 [7]. For most cases, experimental results can be well explained by Ising or Heisenberg interactions among spins [8,11–14]. However, little has been done on the conformational properties of magnetic polymer in solution or melting states. Monte Carlo simulation offers an opportunity to investigate the conformational properties as well as the magnetic properties of magnetic polymer in solution [15,16].

Recently, based on a coarse-grained bond fluctuation model we proposed a ferromagnetic polymer model in good solvents [16]. On the simple cubic lattice, chain's bond length can fluctuate among values 1, $\sqrt{2}$ or $\sqrt{3}$ in unit of the lattice constant. The interactions among monomers are (1) self-avoiding and (2) spatial nearest neighbor ferromagnetic Ising interactions. The model undergoes a magnetic phase transition as well as a spatial conformational collapse transition at the critical temperature $T_c^0 = 1.37 \pm 0.05(J/k_B)$ for infinitely long chains, here the superscript 0 represents the zero field case and J is the spin-coupling. Two scaling exponents $\alpha \approx 0.42$ and $\nu \approx 0.80$ are different from those of two-dimensional (2D) or three-dimensional (3D) Ising models, indicating that the phase transition in the Ising polymer chain model belongs to a different universality class.

In this paper, based on the coarse-grained bond fluctuation ferromagnetic Ising chain model, the dependence of the statistical magnetic and conformational properties of magnetic polymers in dilute solution on an external field is investigated using dynamic Monte Carlo simulations.

2. Model and simulation method

The 3D Ising chain model on the simple cubic lattice is

---

* Corresponding author. Tel./fax: +86-571-879-52424.
E-mail address: hjhchem@yahoo.com.cn (J.H. Huang).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.02.024

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, that 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) 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: $\pm x$, $\pm y$, $\pm z$. 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 pick up a monomer randomly at first and then flip the spin on it according to 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 $h_{\max} = 2.0$, afterwards we make a full cycle by decreasing it to $-h_{\max}$ and at last increasing it to $h_{\max}$ again. The final configuration at the previous field is used as the initial configuration for the subsequent field. For every field h, system is updated for total $500n^2$ MCS and 500 independent samples are recorded with a time interval $\Delta t = n^2$ MCS. 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, the field h and energy E are in unit of J.

3. Results and discussions

3.1. Magnetic property

At first we investigate the dependence of the mean magnetization $\langle M\rangle$ on the external magnetic field h at temperatures $T > T_c^0$ and $T < T_c^0$. The magnetization is defined as the average spin per monomer $M = \frac{1}{n+1}\sum_i \sigma_i$. The chain lengths we simulated are from 50 to 300.

Fig. 1(A) and (B) shows the magnetization-field ($\langle M\rangle$–h) curves for the chain length $n = 200$ at several temperatures. At temperatures below T_c^0, hysteresis in $\langle M\rangle$–h curves is observed. Hysteresis loop has been observed for organic magnetic materials in solid states [10,17,18], however, the roughly rectangle loop shown here indicates a sharp switch between the positive and negative magnetizations in the Ising chain model. Such a steep switch will enable the magnetic polymer to be a good recording material. We find that the coercive force increases with the decrease of temperature, while the remanence is almost independent of the temperature. The remanence is roughly equal to the saturate magnetization $M_s = 1$. At temperatures above T_c^0, however, the hysteresis disappears and the model chain behaves like a paramagnetic material.

For single atom model or non-interaction spin (or angle momentum) model, the paramagnetic $\langle M\rangle$–h curve can be

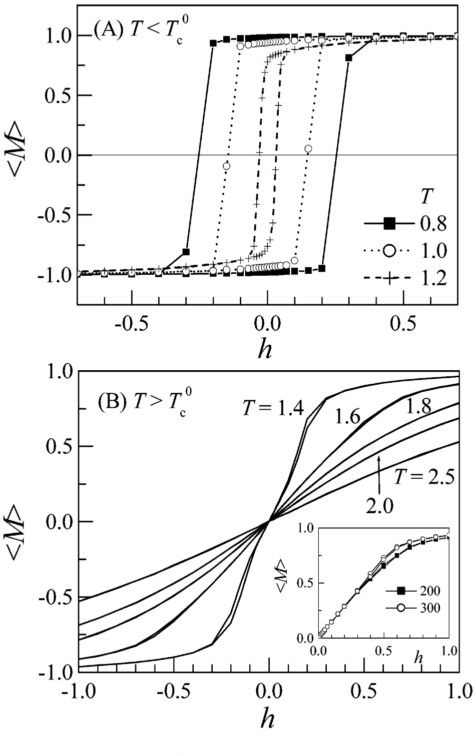

Fig. 1. Magnetization–field ($\langle M\rangle$–h) curves at different temperatures: (A) $T < T_c^0$ and (B) $T > T_c^0$. The chain length is $n = 200$. The inset of (B) presents $\langle M\rangle$–h curves for chain length $n = 200$ and 300 at $T = 1.6$.

described by the Brillouim function $B_j(x)$,

$$\langle M\rangle/M_\mathrm{s} = B_j(x) = \frac{2j+1}{2j}\coth\left[\frac{2j+1}{2j}x\right] - \frac{1}{2j}\coth\left[\frac{1}{2j}x\right] \qquad (2)$$

with parameter $x = \frac{jgh}{k_\mathrm{B}T}$. Here, j is the angle momentum quantum and g the Lande g-factor. For the Ising chain model, the saturation magnetization $M_\mathrm{s} = 1$ and the Lande g-factor $g = 2$ (spin system). Since $h/k_\mathrm{B}T$ is a non-dimensional variable, it is more convenient using $\langle M\rangle - h/k_\mathrm{B}T$ curves than using $\langle M\rangle - h$ ones. The Monte Carlo results are presented in Fig. 2. It is interesting to find that the simulated data fall around $j = 3/2$ curve, indicating that the value j of the whole system is bigger than the local spin value $S = 1/2$. The reason is that there exists spin–spin interactions in the magnetic polymer chain, thus the nearest neighbor spins offer an additional magnetic field, bringing about the local (effective) magnetic field $h_\mathrm{eff} > h$. For example, for the case of the temperature $T = 2.0$ and the chain length $n = 200$, the ratio h_eff/h is about 1.7 for small external field h as shown in the inset of Fig. 2. It is clear that a system with a high effective field h_eff will have large magnetization $\langle M\rangle$, then its $\langle M\rangle - h/k_\mathrm{B}T$ data lie close to high j curve. Thus, one can see from Fig. 2 that the effective field h_eff increases with the increase of the chain length but decreases with the temperature.

3.2. Spatial configuration

We have also studied the dependence of the mean-square radius of gyration $\langle S^2\rangle$ on the external field h for a variety of chain lengths at temperatures $T < T_\mathrm{c}^0$ and $T > T_\mathrm{c}^0$. Some of the results are presented in Fig. 3. At temperatures $T < T_\mathrm{c}^0$, the variation of $\langle S^2\rangle$ is very small with the field but $\langle S^2\rangle - h$ curve shows hysteresis like the $\langle M\rangle - h$ curve shown in Fig. 1(A).

While for the temperature $T = 1.6 > T_\mathrm{c}^0$, the mean-square radius of gyration $\langle S^2\rangle$ is the biggest at zero field and it decreases after introducing an external field h (Fig. 3(B)). This is somewhat a field induced phase transition as having already been discussed in Ref. [15]. The longer the chain length is, the more obvious the decrease of $\langle S^2\rangle$ is. For example, for the chain length $n = 300$, when h increases from 0 to 0.6, $\langle S^2\rangle$ drops from about 200 to 30, and at last it converges to about 20 at large field. We find that the field induced collapse transition is reversible, so the magnetic polymer can be used to design molecular mechanism. From the technical point of view, this is more interesting and in latter discussion we therefore only focus on the situation $T > T_\mathrm{c}^0$.

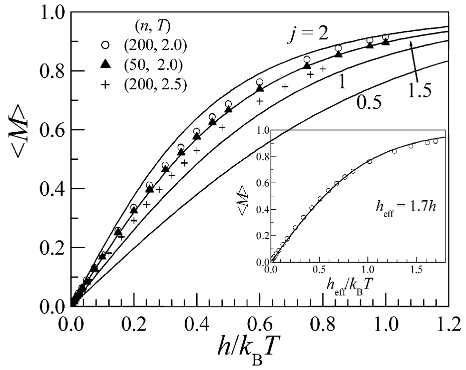

Fig. 2. $\langle M\rangle - h/k_\mathrm{B}T$ data (symbols) for different chain lengths n and different temperatures T. Solid lines are the Brillouin functions $B_j(x)$ for $j = 0.5$, 1, 1.5 and 2, respectively. The insert presents the $\langle M\rangle - h_\mathrm{eff}/k_\mathrm{B}T$ data with $h_\mathrm{eff} = 1.7h$ for the case $n = 200$ and $T = 2.0$.

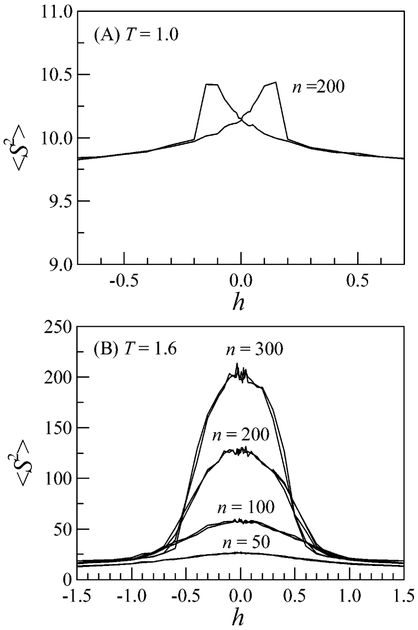

Fig. 3. Dependence of mean-square radius of gyration $\langle S^2\rangle$ on external field h at temperature (A) $T < T_\mathrm{c}^0$ and (B) at $T > T_\mathrm{c}^0$. The chain length and temperature are indicated in the figure.

The dependence of $\langle S^2\rangle/n$ on field h at $T = 1.6$ for different chain lengths is shown in Fig. 4. It is clear that $\langle S^2\rangle/n$ varies more and converges faster for a longer chain. However, if we define the critical field h_c at which $\langle S^2\rangle/n$ (or

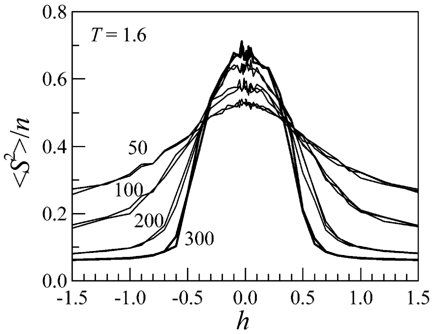

Fig. 4. Dependence of mean-square radius of gyration $\langle S^2\rangle/n$ on external field h at temperature $T = 1.6$ for chain lengths $n = 50$, 100, 200, and 300.

$\langle S^2 \rangle$) varies fastest, i.e. at which the absolute value of slope reaches the maximum, we find that h_c is roughly independent of the chain length. Curves of different chain lengths intersect each other near the critical field h_c. For the temperature $T = 1.6$, h_c is about 0.4. We find h_c increases with temperature, indicating that it needs higher field to shrink the chain at higher temperature, which is in agreement with the results of Ref. [15].

We have also checked the variation of the shape of the chain during the shrinking process of the chain size. It is well known that the instantaneous shape of a polymer chain in dilute solution is not spherical, but is ellipsoidal instead. Ratio $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ was introduced to measure the mean instantaneous shape of flexible polymer chains, here L_1^2, L_2^2, and $L_3^2 (L_1 \le L_2 \le L_3)$ are the eigenvalues of the radius of gyration tensor [19,20]. L_1^2, L_2^2, and L_3^2 are also referred as momentums of three principle axes of chain ellipsoid, respectively. A simple relation between S^2 and these three eigenvalues is $S^2 = L_1^2 + L_2^2 + L_3^2$. Fig. 5(A) presents the response of values $\langle L_1^2 \rangle$, $\langle L_2^2 \rangle$ and $\langle L_3^2 \rangle$ to the field h. Similar to that of $\langle S^2 \rangle$, all these three values have the maximum at zero field $h = 0$, and drop when the field increases. However, the decrease of the largest one $\langle L_3^2 \rangle$ is the most prominent, while the smallest one $\langle L_1^2 \rangle$ changes very little. From Fig. 5(B), the ratios $\langle L_2^2 \rangle / \langle L_1^2 \rangle$ and $\langle L_3^2 \rangle / \langle L_1^2 \rangle$ are plotted as a function of h. We find $\langle L_3^2 \rangle / \langle L_1^2 \rangle$ drops more prominent than $\langle L_2^2 \rangle / \langle L_1^2 \rangle$ does when h increases: the ratio $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ changes from about 1:2.9:14.0 at zero field $h = 0$ to about 1:1.6:2.7 at high field $h = 1.5$. The small value of $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ at high field means that the chain is roughly spherical. We find that the field at which $\langle L_1^2 \rangle$, $\langle L_2^2 \rangle$ and $\langle L_3^2 \rangle$ drops fastest is almost equal to the critical field h_c at which $\langle S^2 \rangle$ drops fastest. So we conclude that the chain undergoes a collapse transition at the critical field h_c.

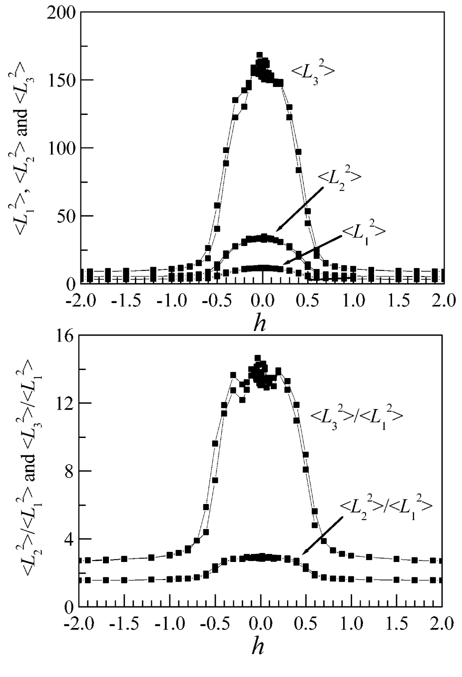

Fig. 5. (A) Dependence of three eigenvalues of the radius of gyration tensor $\langle L_1^2 \rangle$, $\langle L_2^2 \rangle$ and $\langle L_3^2 \rangle (L_1 \le L_2 \le L_3)$ on external field h; (B) Dependence of the ratios $\langle L_2^2 \rangle / \langle L_1^2 \rangle$ and $\langle L_3^2 \rangle / \langle L_1^2 \rangle$ on h. The chain length is 300 and the temperature is 1.6.

4. Conclusion

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 the magnetic and spatial conformational properties are dependent on the external field h. At temperatures below the zero-filed critical temperature T_c^0, hysteresis loop with large remanence are observed, which enable the magnetic polymer to be a good recording material. The magnetization-field curve at $T > T_c^0$ can be described by the Brillouim function with quantum number j bigger than the spin value $S = 1/2$. The spatial configuration changes very little at temperatures $T < T_c^0$, but the chain shrinks obviously with the increase of h at $T > T_c^0$. It is therefore, possible to design molecular mechanism using magnetic polymer. A critical field h_c is defined at which chain undergoes a collapse transition with the spatial configuration (size as well as shape) varies fastest.

Acknowledgements

This work was supported by the National Natural Science Foundation of China under grant number 20204014 and the Zhejiang Provincial Natural Science Foundation of China under grant number 202030.

References

[1] Korshak YV, Medvedeva TV, Ovchinnikov AA, Spector VN. Nature 1987;326:370.

[2] Miller JS, Calabrese JC, Glatzhofer DT, Epstein AJ. J Appl Phys 1988;63:2949.

[3] Torrance JB, Bagus PS, Johannsen I, Nazzal AI, Parkin SSP. J Appl Phys 1988;63:2962.

[4] Cao Y, Wang P, Hu ZY, Li S, Zhang LY, Zhao JG. Solid State Commun 1988;68:817.

[5] Pope M, Swenberg CE. Electronic processes in organic crystal and polymers, 2nd ed. New York: Oxford University Press; 1999.

[6] Takahashi M, Turek P, Nakazawa Y, Tamura M, Nozawa K, Shiomi D, Ishikawa M, Kinoshita M. Phys Rev Lett 1991;67:746.

[7] Rajca A, Wongsriratanakul J, Rajca S. Science 2001;294:1503.

[8] Takahashi M, Turek P, Nakazawa Y, Tamura M, Nozawa K, Shiomi D, Ishikawa M, Kinoshita M. Phys Rev Lett 1991;67:746.

[9] Manners I. Science 2001;294:1664.

[10] Weng J, Jiang LM, Sun WL, Shen ZQ, Liang SQ. Polymer 2001;42: 5491.

[11] James M. J Phys Chem Solids 2000;61:1865.

[12] Clérac R, Miyasaka H, Yamashita M, Coulon C. J Am Chem Soc 2002;124:12837.

[13] Ung VÂ, Couchman SM, Jeffery JC, McCleverty JA, Ward MD, Totti F, Gatteschi D. Inorg Chem 1999;38:365.

[14] Bu XH, Liu H, Du M, Zhang L, Guo YM, Shionoya M, Ribas J. Inorg Chem 2002;41:1855.

[15] Garel T, Orland H, Orlandini E. Eur Phys J 1999;B12:261.

[16] Luo MB, Huang JH. J Chem Phys 2003;119:2439.

[17] Xenikos DG, Müller H, Jouan C, Sulpice A, Tholence JL. Solid State Commun 1997;102:681.

[18] Kou HZ, Gao S, Jin XL. Inorg Chem 2001;40:6295.

[19] Šolc K, Stochmayer WH. J Chem Phys 1971;54:2756.

[20] Šolc K. J Chem Phys 1971;55:335.