

含双噻唑自组装膜的制备及磁性能研究*

徐磊杰 林维红 孙维林** 沈之奎

(浙江大学高分子系高分子科学研究所 杭州 310027)

摘 要 以 2,2'-二氨基-4,4'-联噻唑(DABT)和苯酚为原料合成了新型的偶氮化合物 2,2'-对苯酚偶氮基-4,4'-联噻唑(BTDP), 将其与聚二甲基二烯丙基氯化铵(PDDA)在聚乙烯(PE)膜上进行层层自组装, 并与过渡金属离子进行了配位. UV-Vis 和 FT-IR 表征发现这种膜可以均匀的进行组装, 且能较好的与金属离子配位. 多功能材料物理特性测量系统(physical property measurement system, PPMS)测定配合物的磁性能, 测试结果表明, 与两者溶液直接混合后沉淀配合物的磁性相比, 在 PE 膜上形成的自组装膜配合物的磁性能有较大幅度的提高.

关键词 2,2'-二氨基-4,4'-联噻唑, 自组装, 金属配合物, 磁性能

由于磁性高分子具有广阔的应用前景, 近年来有机和有机金属高分子磁性材料合成及理论的研究, 越来越引起国内外科学家的重视. 1991 年 Allemand 等^[1]首次报道 $C_{60} \cdot TDAE_{0.86}$ 在 5 K 以下是有机软铁磁体, 引起各国科学家的极大兴趣. 1998 年 Hoffmann 等^[2]从理论上提出含有 C、N 和 S 的五元杂环聚合物会表现出磁有序. 近年来, 孙维林等^[3~6]制备了一系列含双噻唑的聚席夫碱, 并与过渡金属离子和稀土金属离子配合, 得到其金属配合物并研究它们的磁性能.

自从 Decher^[7]报道了聚电解质通过静电相互作用制备多层超薄膜以来, 静电自组装技术受到越来越多的关注^[8~10]. 带有相反电荷的聚电解质与聚电解质或聚电解质和多端带有相同电荷的小分子, 可交替沉淀在基片(云母、石英等)上, 形成超薄有序的自组装膜.

含双噻唑的芳杂环与过渡金属离子有良好的配位能力, 而静电自组装能形成有序的结构. 因此为了进一步地探寻高性能, 更优异的新型有机磁性材料, 本文设计并合成了含有双噻唑环且两端能形成负电荷的偶氮化合物, 与带有正电荷的聚电解质进行自组装形成有序结构, 从而产生更好的磁性.

1 实验部分

1.1 试剂

聚二甲基二烯丙基氯化铵(PDDA) 20%水溶

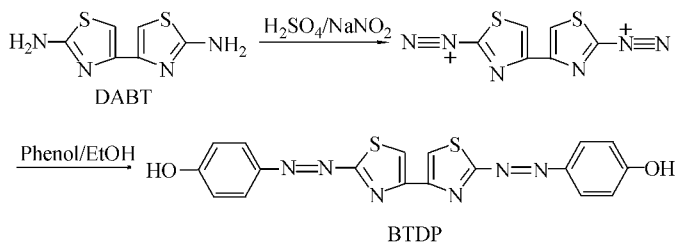
液, AR, Aldrich 公司的产品. 苯酚, CP, 国药集团化学试剂有限公司. 氢氧化钠, AR, 杭州化学试剂有限公司. $NaNO_2$, CP, 国药集团化学试剂有限公司. $NiSO_4 \cdot 6H_2O$, AR, 上海横信化学试剂有限公司. $CuSO_4 \cdot 5H_2O$, CP, 浙江杭州萧山化学试剂厂. 2,2'-二氨基-4,4'-联噻唑(DABT)按文献^[11]方法制备, 并重结晶提纯.

1.2 2,2'-对苯酚偶氮基-4,4'-联噻唑(BTDP)的合成

BTDP(示意式 1)根据 Jensen 的类似方法合成^[12]. 将 2.0 g DABT(10 mmol)溶解在 10 mol/L 的硫酸(50 mL)中形成的溶液加入到装有机械搅拌、温度计和恒压滴液漏斗的 250 mL 三口烧瓶中, 在冰盐浴中冷却到 0℃. 不断搅拌下将 1.4 g (20 mmol) $NaNO_2$ 溶于 10 mL 水形成的溶液冷却后缓缓滴入上述溶液中. 控制滴加速度, 使滴加在 30 min 内完成, 所得红色重氮盐溶液再搅拌 0.5 h, 用淀粉 KI 试纸测试反应终点. 待重氮化进行完全后, 在剧烈的搅拌下, 将 2 g 苯酚(20 mmol)溶于 50 mL 乙醇形成的溶液在 0.5 h 内匀速滴加到上述重氮盐溶液中. 滴加完成后, 再搅拌 1 h, 然后放置过夜, 整个过程体系温度不要超过 5℃. 将所得红色固体过滤, 大量水洗, 再在 50℃ 下真空干燥 20 h. 将所得固体在乙醇中重结晶, 所得红色片状晶体在 50℃ 真空干燥. 产量为 2.6 g (产率 66%).

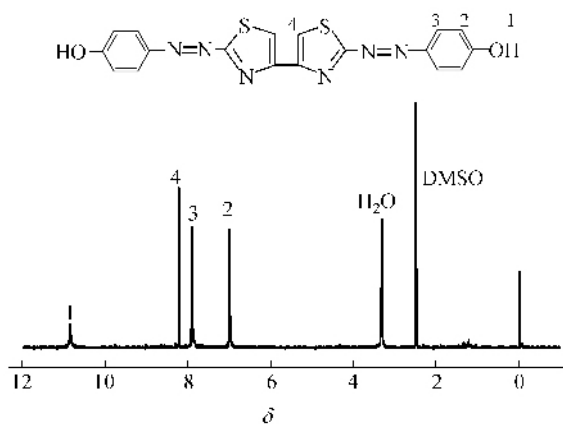
* 2007-04-10 收稿, 2007-05-11 修稿. 国家自然科学基金资助项目(基金号 20674071 和 20434020); ** 通讯联系人, E-mail:

opl_sunwl@zju.edu.cn



Scheme 1 Synthetic route for BTDP

BTDP 的 $^1\text{H-NMR}$ (δ , $\text{DMSO}-d_6$) 如图 1, 各 H 的化学位移为 10.860 (2H), 8.226 (2H), 7.908 ~ 7.930 (4H), 6.997 ~ 7.091 (4H), 表明与实验结果相符.

Fig. 1 $^1\text{H-NMR}$ spectrum of BTDP

1.3 PE-(PDDA/BTDP) $_n$ 多层自组装膜及其配合物的制备

1.3.1 PE 膜表面的处理 将纯净的 PE 膜用 $\text{CrO}_3/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ 氧化成 PE-COOH 膜^[13].

1.3.2 PE-(PDDA/BTDP) $_n$ 多层自组装膜的制备

将 PE-COOH 膜在 2×10^{-3} mol/L 的 PDDA 水溶液中浸泡 30 min 后, 用去离子水洗 3 次, 吹干再浸入到 pH = 9 的 5×10^{-3} mol/L 的 BTDP 水溶液中, 30 min 后取出并清洗吹干, 获得 PE-(PDDA/BTDP) $_1$ 的组装膜. 依次交替操作, 便可制得不同层数的 PE-(PDDA/BTDP) $_n$ 自组装膜.

1.3.3 PE-(PDDA/BTDP- M^{2+}) $_n$ 多层自组装配合物膜的制备 将 PE-COOH 膜在 2×10^{-3} mol/L 的 PDDA 水溶液中浸泡 30 min 后, 用去离子水洗 3 次, 吹干再浸入到 pH = 9 的 5×10^{-3} mol/L 的 BTDP 水溶液中, 30 min 后取出并清洗吹干; 最后将获得的 PE-(PDDA/BTDP) $_n$ 多层自组装膜分别浸入 NiSO_4 和 CuSO_4 的水溶液中, 20 h 后取出清

洗以除去表面物理吸附的金属离子, 吹干, 按此方法循环进行.

1.4 PDDA/BTDP- M^{2+} 沉淀配合物的制备

把 2 g BTDP 溶解于 20% 的氢氧化钠水溶液中, 加入 4 g 20% PDDA 的水溶液, 立即产生红黑色的固体沉淀. 将所得沉淀物过滤, 用大量水、甲醇洗涤. 然后在 50°C 下真空干燥两天.

将 0.5 g 沉淀物和 50 mL DMSO 加入到干燥的通有氮气的单颈瓶中, 然后加入两倍摩尔数的过渡金属硫酸盐. 氮气保护下, 于 50°C 下搅拌反应 24 h, 冷却, 倒入蒸馏水中沉淀, 过滤, 并用大量的水和甲醇洗涤, 以除去吸附的过渡金属离子. 然后产物在 50°C 下真空干燥 24 h.

1.5 产物的表征

产物的红外光谱均采用 KBr 压片法, 由 BRUKER VECTOR 22 红外光谱仪测得; $^1\text{H-NMR}$ 用 BRUKER AVANCE AMX2400 核磁共振仪测定; 自组装膜层数用 UV 23150 型紫外-可见分光光度仪测定; 配合物的磁性能采用 PPMS29T (QUANTUM DESIGN) 测量仪测定, 温度范围为 2 ~ 300 K, 磁场强度范围为 -4×10^6 A/m ~ 4×10^6 A/m.

2 结果和讨论

2.1 PE-(PDDA/BTDP) $_n$ 自组装膜及其配合物表征

PDDA 为带有正电荷的聚电解质, 而 BTDP 在碱性环境中两端带有负电荷, 两者通过静电作用能够在基片上形成多层自组装膜. BTDP 含有苯环和噻唑环, 在 UV-Vis 光谱中有特殊的吸收峰. 图 2 (a) 为不同层数 PE-(PDDA/BTDP) $_n$ 自组装膜的 UV-Vis 光谱. 从图中可以看出随着层数的增加, UV-Vis 的吸收强度也有规律的增长. 在 413 nm 处 BTDP 中噻唑环的特征吸收强度随层数的增加均匀增加 (图 2a 插图中所示的曲线), 表明组装膜很均匀.

BTDP 中含有联噻唑环,因此能螯合金属离子^[14],其可能螯合情况的结构示意图如图 3.图 2 (b)为 PE-(PDDA/BTDP-Ni²⁺)_n 自组装膜的 UV-Vis 光谱图.从图中可看出在 413 nm 处的吸收峰在螯

合 Ni²⁺ 后移动到了 400 nm 处.这是由于 Ni²⁺ 离子配位作用使联噻唑环的振动需要更多的能量.自组装膜螯合 Cu²⁺ 后吸收峰的也有类似移动.

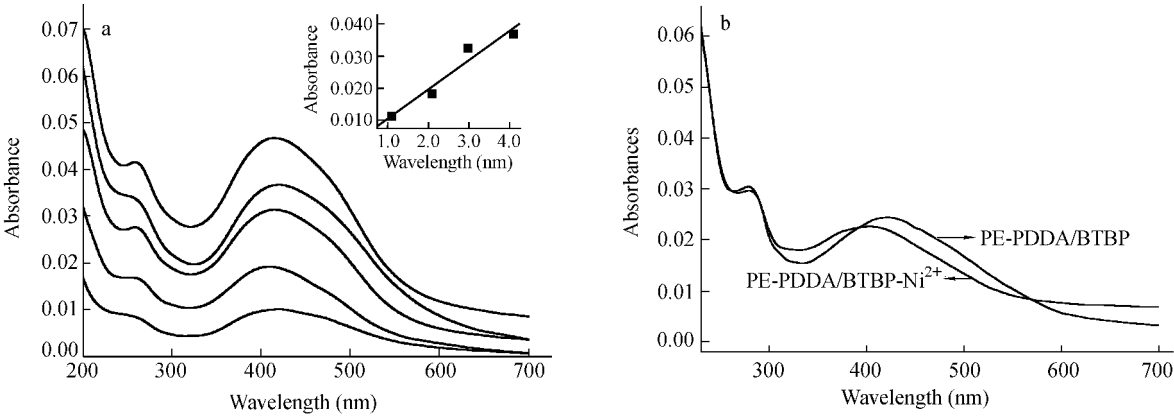


Fig. 2 UV-Vis absorption spectra of the following multilayered films on PE substrate
a) PE-(PDDA/BTDP)_n bilayers with different numbers. Shown in the insert are the plots of the absorbance at 413 nm versus the number of PDDA/BTDP bilayer ; b) PE-PDDA/BTDP and PE-PDDA/BTDP-Ni²⁺

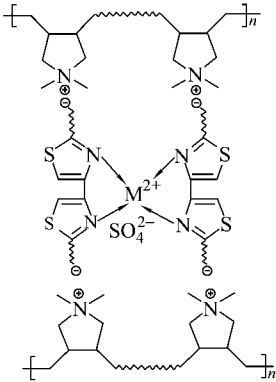


Fig. 3 Simplified schematic representation of the first eight steps in assembling the multilayered film PE-(PDDA/BTDP-M²⁺)_n, including possible structure in the film, M²⁺ = Ni²⁺, Cu²⁺

图 4 是关于 PE-(PDDA/BTDP)_n 自组装膜的红外谱图. PE 在氧化后形成了 PE-COOH,图中在 1710 cm⁻¹ 处的羧基峰可以很好证明这一点.从图中还可看出 PE-(PDDA/BTDP)₂₅ 在 1585 cm⁻¹ 处的吸收峰为 BTDP 的共轭 C=C 吸收峰,说明在 PE 膜上确实形成了自组装膜.而 PE-(PDDA/BTDP-Ni²⁺)₂₅ 和 PE-(PDDA/BTDP-Cu²⁺)₂₅ 的共轭 C=C 吸收峰分别在 1597 cm⁻¹ 和 1596 cm⁻¹ 处,这可能是由于与 Ni²⁺、Cu²⁺ 配位后,影响了键能,使得该吸收峰发生了偏移.

2.2 PE-(PDDA/BTDP-M²⁺)_n 自组装膜与 PDDA/BTDP-M²⁺ 沉淀配合物的磁性能比较

在测定 PE-(PDDA/BTDP)_n 自组装膜磁性能

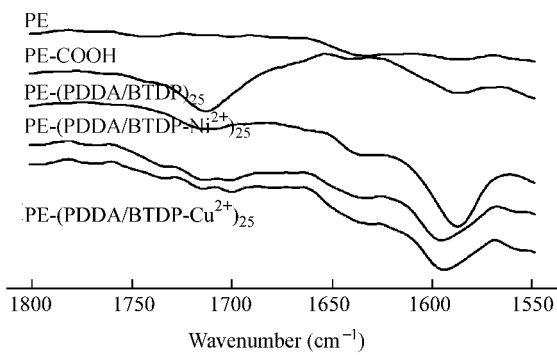


Fig. 4 IR spectrum of PE, PE-COOH, PE-(PDDA/BTDP)₂₅, PE-(PDDA/BTDP-Ni²⁺)₂₅ and PE-(PDDA/BTDP-Cu²⁺)₂₅

之前,我们先测定了基底 PE-COOH 膜的磁性能.图 5 为外加磁场为 2.39 × 10⁶ A/m 时,PE-COOH 膜的磁化率的倒数(χ⁻¹)以及磁化率与温度的乘积(χT)与温度(T)的关系曲线图,从图中可以看出该磁化率为负值,且在低温下随温度变化而变化,所以 PE-COOH 膜是一种抗磁体.

图 6 所示为外加磁场为 2.39 × 10⁶ A/m 时, PE-(PDDA/BTDP-Ni²⁺)₂₅ 多层自组装膜和 PDDA/BTDP-Ni²⁺ 沉淀配合物的磁性能比较图.图 6(a)是两者的磁化强度和温度的关系曲线.由图中可以看到,两者的变化较为相似,都是随着温度的降低,磁化率先是略有增加,但是不明显.在较低温度时,磁化强度发生突变,急剧增大,且 PE-(PDDA/BTDP-Ni²⁺)₂₅ 的磁化强度比 PDDA/BTDP-

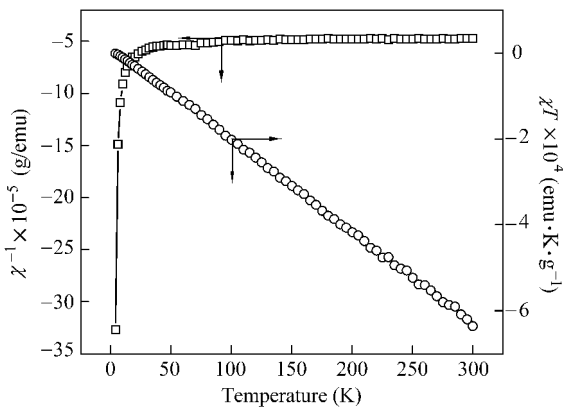
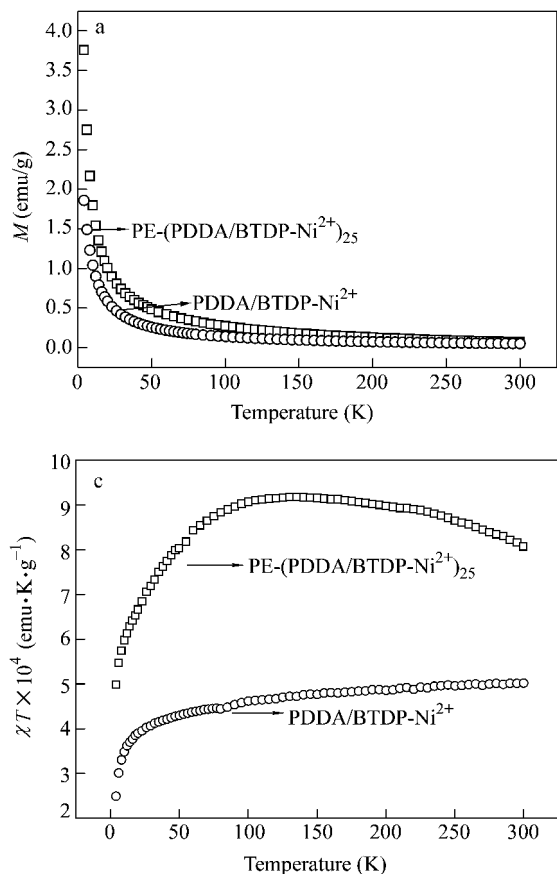


Fig. 5 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for the oxidized polyethylene (PE-COOH) film at an applied field magnetic field of 2.39×10^6 A/m



Ni^{2+} 的磁化强度要增加的快.表明在这温度附近,物质的磁性质发生了本质性的变化,可能在低温的条件下物质进入了磁有序状态,而层层自组装膜使其更为有序.图 6(b)、6(c)是两者的磁化率的倒数(χ^{-1})以及磁化率与温度的乘积(χT)与温度(T)的关系曲线.从图 6(b)中可以看出磁化率的倒数(χ^{-1})随着温度的升高而增加,用居里-外斯定律拟合时,在高温区几乎是一条直线,这意味着在高温区主要以顺磁为主,其延长线与温度轴的交点为居里-外斯温度.由图可知 PE-(PDDA/BTDP- Ni^{2+})₂₅ 的居里-外斯温度为 128 K,表明在低温下主要为铁磁性相互作用.而 PDDA/BTDP- Ni^{2+} 的居里-外斯温度为 -10 K,表明在低温下主要为反铁磁性相互作用.从图 6(b)中也能说明这一

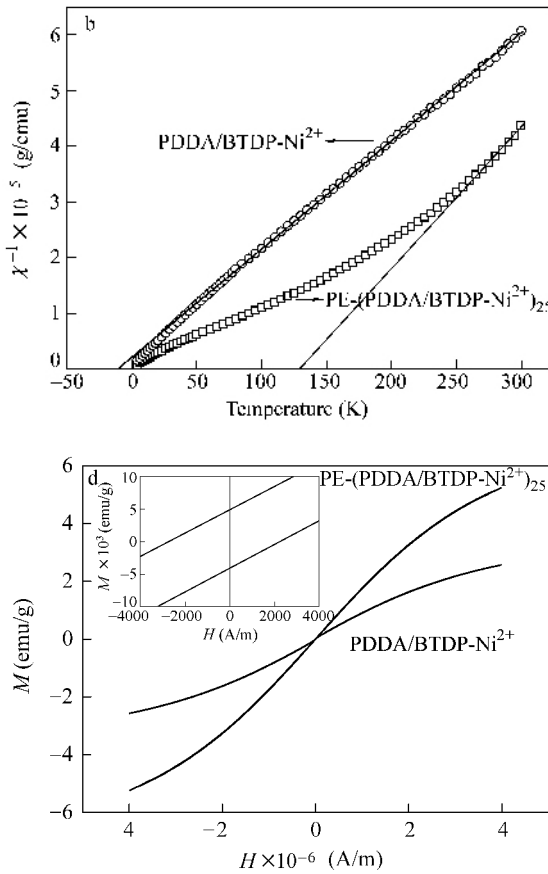


Fig. 6 (a) Magnetization (M) versus temperature for PE-(PDDA/BTDP- Ni^{2+})₂₅ and PDDA/BTDP- Ni^{2+} ; (b) Reciprocal susceptibility (χ^{-1}) versus temperature (T) for the PDDA/BTDP- Ni^{2+} deposit complexes and the multilayered film PE-(PDDA/BTDP- Ni^{2+})₂₅, the straight line is a fit to the Curie-Weiss law; (c) Product magnetic susceptibility and temperature (χT) for PDDA/BTDP- Ni^{2+} deposit complexes and the multilayered film PE-(PDDA/BTDP- Ni^{2+})₂₅; (d) Hysteresis loop at $T = 4$ K for the PDDA/BTDP- Ni^{2+} deposit complexes and the multilayered film PE-(PDDA/BTDP- Ni^{2+})₂₅

Inset :expanded view of the region from -8000 to 8000 A/m of multilayered film PE-(PDDA/BTDP- Ni^{2+})₂₅

点,PE-(PDDA/BTDP- Ni^{2+})₂₅ 的温度乘积(χT)与温度(T)的关系曲线中出现了最高点,这是铁磁性物质所具有的特征.而 PDDA/BTDP- Ni^{2+} 的该关系

曲线中并没有最高点,而是随着温度的降低,配合物磁化率和温度的乘积不断降低,在高温区降低得比较缓慢,在低温下降低的趋势越来越明

显,这是反铁磁性物质所具有的特征.说明层层自组装产生的有序结构使得居里-外斯温度大大提高.图 6(d)是两者的磁滞回线,曲线呈 S 形,插图为 PE-(PDDA/BTDP- Ni^{2+})₂₅ 在 $-4000\text{ A/m} \sim 4000\text{ A/m}$ 区间的放大图.表 1 是综合了 4 种物质的磁性能,从表中看出 PE-(PDDA/BTDP- Ni^{2+})₂₅ 的磁饱和和强度 ($M_s = 5.3\text{ emu/g}$) 明显大于 PDDA/BTDP-

Ni^{2+} 磁饱和强度 ($M_s = 2.6\text{ emu/g}$),说明自组装膜的有序性有利于磁饱和强度的提高.两者的剩余磁化强度 (M_r) 分别为 0.0049 emu/g 和 0.0035 emu/g ,矫顽力 (H_c) 分别为 2228.17 A/m 和 2307.75 A/m .说明两者都具有较小的磁损耗,是一种软磁性物质^[11].

Table 1 Magnetic properties of multilayer films and deposit complexes

Complex	Relative saturation magnetization at	Remanence magnetization at	Coercivity at 4 K	Curie-Weiss temperature
	4 K (emu/g)	4 K (emu/g)	(A/m)	(K)
PE-(PDDA/BTDP- Ni^{2+}) ₂₅	5.30	0.0049	2228.17	128
PDDA/BTDP- Ni^{2+}	2.60	0.0035	2307.75	-10
PE-(PDDA/BTDP- Cu^{2+}) ₂₅	1.58	0.0005	725.46	70
PDDA/BTDP- Cu^{2+}	1.03	0.0066	6366.20	-145

图 7 所示为外加磁场为 $2.39 \times 10^6\text{ A/m}$ 时, PE-(PDDA/BTDP- Cu^{2+})₂₅ 多层自组装膜和 PDDA/BTDP- Cu^{2+} 配合沉淀物的磁性能比较图.从图中

发现两者的变化比较与上部分 PE-(PDDA/BTDP- Ni^{2+})₂₅ 多层自组装膜和 PDDA/BTDP- Ni^{2+} 配合沉淀物的变化比较相类似,其主要磁性能详见表 1.

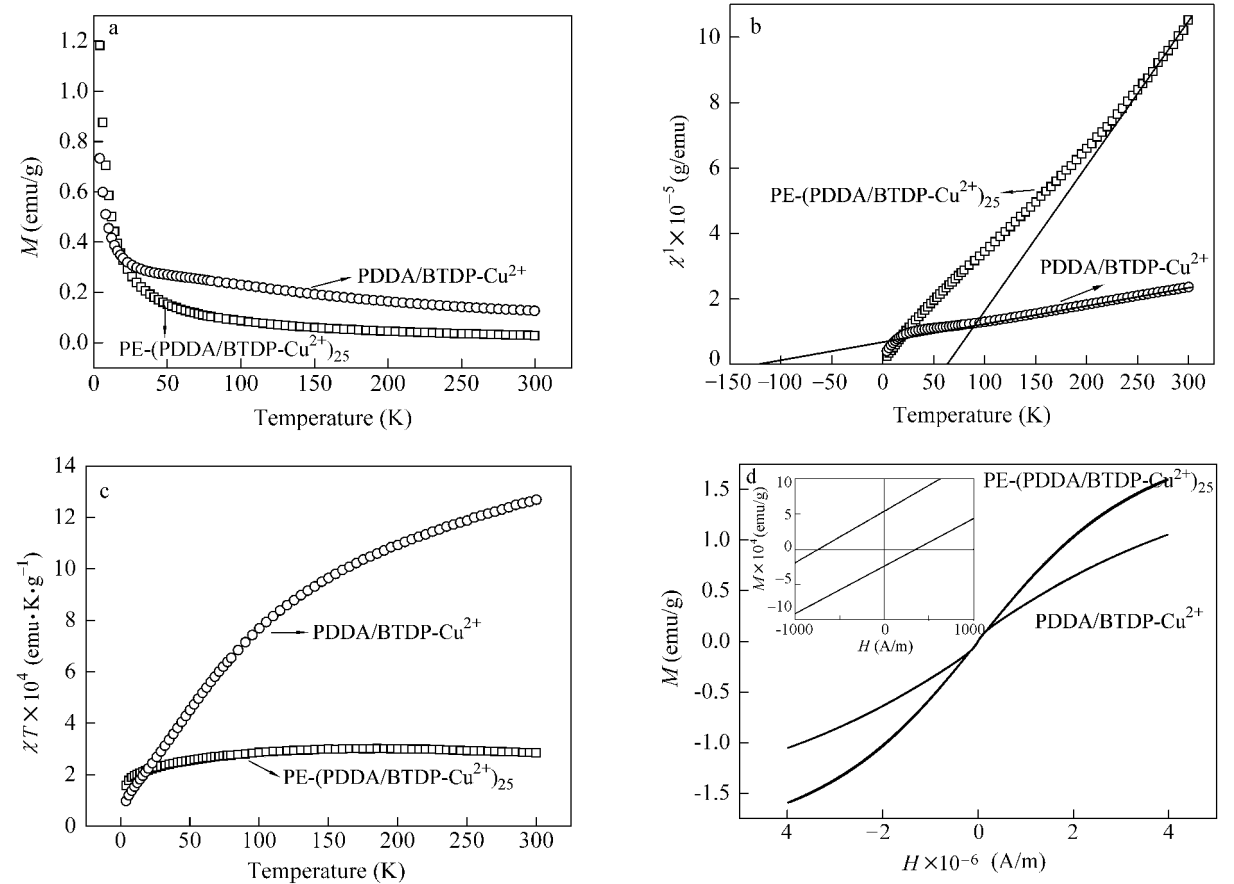


Fig. 7 (a) Magnetization (M) versus temperature for PE-(PDDA/BTDP- Cu^{2+})₂₅ and PDDA/BTDP- Cu^{2+} ; (b) Reciprocal susceptibility (χ^{-1}) versus temperature (T) for the PDDA/BTDP- Cu^{2+} deposit complexes and the multilayered film PE-(PDDA/BTDP- Cu^{2+})₂₅, the straight line is a fit to the Curie-Weiss law; (c) Product magnetic susceptibility and temperature (χT) for PDDA/BTDP- Cu^{2+} deposit complexes and the multilayered film PE-(PDDA/BTDP- Cu^{2+})₂₅; (d) Hysteresis loop at $T = 4\text{ K}$ for the PDDA/BTDP- Cu^{2+} deposit complexes and the multilayered film PE-(PDDA/BTDP- Cu^{2+})₂₅ Inset: expanded view of the region from -2000 A/m to 2000 A/m of multilayered film PE-(PDDA/BTDP- Cu^{2+})₂₅

通过以上的磁性能的比较分析,发现通过层层自组装而形成的自组装膜其磁性能与两者通过简单混合而形成的沉淀配合物的磁性能相比,有了较大的提高.这可能是由于自组装膜具有良好的有序结构,使得未成对电子之间形成了更好的相互交换作用,这种作用使未成对电子趋向同方

向排列.以上的研究可以得出分子排列结构对磁性能有很大影响,为今后设计磁性高分子提供了很好的研究依据.

致谢 感谢浙江大学分析测试中心冯春木老师的帮助.

REFERENCES

- 1 Allemand P M, Khemani K C, Koch A, Wudl F, Holczer K, Donovan S, Gruner G, Thompson J D. *Science*, 1991, 253 :301 ~ 303
- 2 Genin H, Hoffmann R. *Macromolecules*, 1998, 31 :444 ~ 455
- 3 Sun Weilin(孙维林), Shen Zhiquan(沈之荃). *Acta Polymerica Sinica(高分子学报)*, 2005, (5) :641 ~ 648
- 4 Tang Jianbin(唐建斌), Sun Weilin(孙维林), Jiang Liming(江黎明), Shen Zhiquan(沈之荃). *Chemistry(化学通报)*, 2004, (1) :30 ~ 32
- 5 Liu Zhichao(刘志超), Sun Weilin(孙维林), Liu Shang(刘爽), Shen Zhiquan(沈之荃). *Acta Polymerica Sinica(高分子学报)*, 2004, (5) :667 ~ 671
- 6 Lin Caipin(林彩萍), Sun Weilin(孙维林), Jiang Liming(江黎明), Shen Zhiquan(沈之荃). *Acta Polymerica Sinica(高分子学报)*, 2003, (6) :826 ~ 830
- 7 Decher G, Hong J D. *Macromol Chem Macromol Symp*, 1991, 46 :321 ~ 327
- 8 Tang Liming(唐黎明), Fang Yu(方宇), You Hu(由虎). *Acta Polymerica Sinica(高分子学报)*, 2005, (4) :625 ~ 628
- 9 Pascal Y, Vuillaume C, Geraldine B. *Macromolecules*, 2003, 36 :6378 ~ 6388
- 10 Zhao W, Xu J J, Shi C G, Chen H Y. *Langmuir*, 2005, 21 :9630 ~ 9634
- 11 Sun W L, Gao X S, Lu F C. *Chinese J Polym Sci*, 1997, 15 :325 ~ 331
- 12 Jensen B S. *Acta Chemica Scandinavica*, 1960, 14 :927 ~ 932
- 13 Rasmussen J R, Stedronsky E R, Whitesides G M. *J Am Chem Soc*, 1977, 99(14) :4736 ~ 4745
- 14 Weng Jian, Sun W L, Jiang L M. *Macromolecular Rapid Communications*, 2000, 21 :1099 ~ 1102

STUDIES ON PREPARATION AND MAGNETIC PROPERTIES OF SELF-ASSEMBLED MULTILAYER FILMS CONTAINING BITHIAZOLE RINGS

XU Leijie, LIN Weihong, SUN Weilin, SHEN Zhiquan

(Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027)

Abstract Organic magnetism is a rapidly developing field that combines the skills of experimental and theoretical scientists in many areas of chemistry and physics. Compared with inorganic ferromagnet, the organic ferromagnet exhibits the characteristics of structural diversities, low density, and readily processing. In addition, layer-by-layer (LBL) assembled multilayered films have received considerable interest because they allow fabrication of supramolecules with tailored architecture and properties. The design and preparation of organic soft ferromagnets by self-assembling is reported in this article. 4,4'-(4,4'-Bithiazole-2,2'-diylbis(diazene-2,1-diyl)) diphenol (BTDP) was first synthesized from phenol and 2,2'-diamino-4,4'-bithiazole (DABT), and the structure of BTDP was characterized by $^1\text{H-NMR}$. The hydroxyls of the BTDP provide anions while the poly(diallyldimethylammonium chloride) (PDDA) provides cations, so the layer-by-layer self-assembling of BTDP with PDDA was carried out based on the electrostatic interaction on the polyethylene (PE) surface with carboxylic acid groups ($-\text{COOH}$). BTDP coordinates with transition metal ions since two nitrogen atoms in the thiazole rings and metal ions can provide stable five-member rings. Therefore, the complexes of assembled multilayer films ($\text{PE-(PDDA/BTDP-M}^{2+})_n$) were also

prepared *via* layer-by-layer assembly. The assembling process was monitored by UV-Vis spectroscopy. The linear increase of the absorbance at 413 nm with increasing the layer number indicates a process of uniform assembling. The structure of the complexes was characterized by FTIR, which suggests that the chelation has taken place demonstrated by the shift of the characteristic absorption band. In addition, the BTDP and PDDA deposition obtained by mixing their solutions could react with transition metal ions to form their metal complexes, which was also characterized by FTIR. The magnetic properties of these complexes were measured using a Physical Property Measurement System (PPMS-9), which included magnetization versus temperature, magnetization versus applied field, magnetic susceptibility versus temperature and magnetic hysteresis. The temperature is ranged from 4 to 300 K, and the intensity of magnetic field is in the range of $-4 \times 10^6 \sim 4 \times 10^6$ A/m. It was found that these complexes were organic soft magnets and had typical "S" shaped magnetic hysteresis loops. The saturation magnetization of the complex of assembled multilayer film $\text{PE-(PDDA/BTDP-Ni}^{2+}\text{)}_{25}$ is 5.30 emu/g, and the paramagnetic Curie temperature is 128 K, while the remanence magnetization and coercivity are 0.0049 emu/g and 2228.17 A/m, respectively. The results show that $\text{PE-(PDDA/BTDP-Ni}^{2+}\text{)}_{25}$ is an organic soft ferromagnet at low temperatures. The magnetic properties of the multilayer film for $\text{PE-(PDDA/BTDP-Cu}^{2+}\text{)}_{25}$ is similar with those for $\text{PE-(PDDA/BTDP-Ni}^{2+}\text{)}_{25}$. The saturation magnetization of deposit complex PDDA/BTDP-Cu^{2+} is 2.60 emu/g, and the paramagnetic Curie temperature is -10 K, while the remanence magnetization and coercivity are 0.0035 emu/g and 2307.75 A/m, respectively. The results show that $\text{PE-(PDDA/BTDP-Cu}^{2+}\text{)}_{25}$ is an organic soft antiferromagnet at low temperatures. The magnetic properties of deposition for PDDA/BTDP-Cu^{2+} are similar with those for PDDA/BTDP-Ni^{2+} . In comparison, it was proved that the magnetic properties of multilayer self-assembled films were much better than those of deposited complexes. The strong ferromagnetism of the multilayered film may arise from the exchange interaction of the transition metal ions in the ligands which show a well-ordered 3-D network structure.

Keywords 2,2'-Diamino-4,4'-bithiazole, Self-assemble, Metal complexes, Magnetic property