

The Synthesis of Copolymer–Cu Coordinates and Its Catalysis to Methyl Methacrylate

Jianmei Lu,^{1,2} Jianfei Wu,² Lihua Wang,² Shechun Yao²

¹Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006 People's Republic of China
²Jiangsu Polytechnic University, Changzhou 213016, People's Republic of China

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ABSTRACT: The copolymerization of methacrylic acid, 2-(dimethylamino) ethyl ester (DM), and allythiourea (AT) was studied under microwave, and the copolymer–copper coordinates Cu-P(DM-Co-AT) was synthesized by the coordination between Cu²⁺ and the copolymer. IR, X-ray photoelectron spectroscopy, and electronic spin resonance were used to analyze the structure of Cu-P(DM-Co-AT). The results showed that the inherent viscosity of the copolymer obtained by microwave irradiation can be the maximum of

37.75 ml/g, and the productive rate can be 92%. The obtained Cu-P(DM-Co-AT) can heterogeneously catalyze the polymerization of methyl methacrylate at room temperature. The maximal molecular weight of poly(methyl methacrylate) was 1,400,000. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2072–2075, 2005

Key words: catalysis; microwave irradiation; copolymer; coordinate

INTRODUCTION

In 1986, some organic reactions under microwave irradiation were reported by Gedye et al.¹ and Giguere et al.² After the application of microwave irradiation in organic reactions, it also caused researchers to study the polymeric reaction under microwave irradiation and got a certain progress. In the area of synthesis of polymer, microwave has been used to carry out the radical polymerization of vinyl monomers such as 2-hydroxy ethyl methacrylate,³ styrene,⁴ methyl methacrylate (MMA, China Medicine Group, Shanghai Chemical Reagents Corporation, Shanghai, China);⁵ and the curing of polymer such as epoxy resins and polyurethane,^{6–10} as well as the imidization of polyamic acids (PAA).^{11,12} During the course of our studies, we reported on the microwave irradiation, addition polymerization, and condensation polymerization.^{13–17} Microwave also has an obvious effect in carrying out the metal–organic reactions, such as synthesis of some metal complex; it took only minutes under microwave conditions, whereas it will take several hours, even more than 100, by traditional means.¹⁸ In the Chemical Department of London Loyal Institute, Michael and Mingos¹⁹ realized the preparation of self-assembled PMC in one step by utilizing the microwave oven. This was the first exam-

ple of self-assembly based on the coordinate bond and hydrogen bond in one step.

In this article, the vinyl monomers were used to synthesize PMC, which contained the electron-donating atoms N and S. Because N and S are located on the side chain, the PMC obtained was a side-chain-type metal complex. The PMC has the characteristics of both organic polymer and inorganic metals. It is a new type of polymer, the novel structure and singular performance of which have attracted much attention. In this article, the catalytic function of Cu-P(DM-Co-AT) was studied.

EXPERIMENTAL

Base material

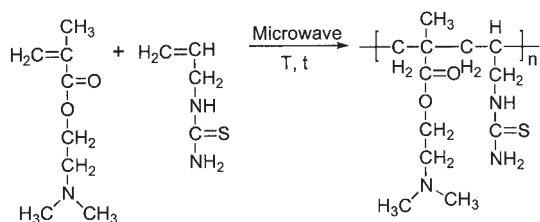
2-(Dimethylamino) ethyl ester (DM; China Medicine Group, Shanghai Reagents Corporation) allythiourea (AT; China Medicine Group, Shanghai Reagents Corporation), MMA, methyl alcohol, chemically pure, tetrahydrofuran, sodium sulfite (China Medicine Group, Shanghai Reagents Corporation), blue vitriol, hydrochloric acid, analytically pure, were used as received.

Synthesis device

The Jianhua microwave, KS2163, with a maximum output power of 850 W, was refitted. The microwave oven electric current could be adjusted and read continuously by using a voltage regulator, which was installed outside of the oven. The reaction device was installed inside the oven.

Correspondence to: J. Lu (lujm@suda.edu.cn).

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Scheme 1 The route of the polymerization.

Procedure of experiment

The copolymerization of DM and AT under microwave irradiation

Copolymerization of DM and AT under microwave irradiation is shown in Scheme 1. DM and AT were added prorate into a three-necked bottle and put into a refitted microwave device; the mixture was degassed with N_2 for 30 min. Then the microwave irradiation reaction started, protected with N_2 at all times. The temperature was controlled at 80–90°C; and the reaction power was adjusted by the regulation of electric current. After a set time, the mixture was taken out and treated with petroleum ether and absolute ethyl alcohol. The brown and mucous polymer was obtained and was dried up until a constant weight under vacuum at low temperature.

Synthesis of Cu-P(DM-Co-AT)

DM : AT = 10 : 1 (mole ratio) was added into a three-necked bottle, degassed with N_2 for 30 min, and then a certain blue vitriol was added, which started the microwave irradiation reaction. The reaction power was adjusted by the regulation of electric current around 15 mA. After a set time, the mixture was taken out and treated with methyl alcohol to form a solid-liquid mixture. After it was poured out, a certain blue vitriol was added to make the coordination. After centrifugal separation, the Cu^{2+} that did not coordinate with polymer with deionized water was

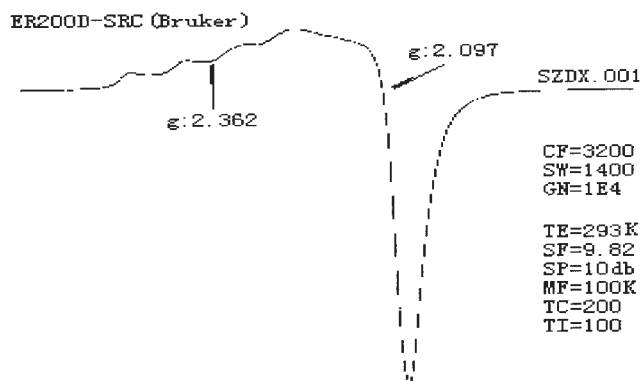


Figure 1 ESR of Cu-P(DM-Co-AT).

TABLE I
Effect of Reaction Time on the Monomer Conversion

Reaction time (h)	2	4	6	8	10	12
Monomer conversion	4.53	25.0	35.7	42.0	42.6	40.8

washed out. The solid was dried to constant weight under vacuum at a low temperature and ground into powder, and PMC was obtained.

The polymerization of vinyl monomer MMA catalyzed by the Cu-P(DM-Co-AT)

A certain vinyl monomer MMA was weighed and added into a conical bottle, and then a certain weight ratio of Cu-P(DM-Co-AT)/ Na_2SO_3 aqueous was added. After a certain time, the solution was poured into methyl alcohol, which contained a certain concentration hydrochloric acid, and the poly (methyl methacrylate) (PMMA) was separated out, filtered with deionized water, and then dissolved in THF. The process was repeated three times. A certain hydrochloric acid was added to destroy the PMC, causing the Cu^{2+} to dissolve into the water and making the polymer metal complex (PMC) separate from PMMA. PMMA was dried up to a constant weight; its viscosity determined, and GPC conducted.

Measurement

FT-IR spectra of copolymer were recorded on a PerkinElmer 577 FT-IR Spectrometer. Electron spin resonance (ESR) spectra of Cu-P(DM-co-AT) was performed on Bruker ER2000-SRC spectrometer. X-ray photoelectron spectroscopy of Cu-P(DM-co-AT) was recorded on NP-1 XPS spectrometer (Shenyang, China). The molecular weight of PMMA was determined by WATERS 150c Gel chromatogram (GPC).

RESULTS AND DISCUSSION

The copolymerization of DM and AT under microwave irradiation

The reactive mode

The influence of microwave irradiation time to the polymer conversion. As shown in Figure 1, when DM : AT = 10

TABLE II
Effect of Microwave Irradiation Power on Inherent Viscosity of Polymer

Microwave irradiation power (mA)	10	20	30	40	50	60
Inherent viscosity (ml/g)	21.419	21.778	20.838	20.503	19.681	18.573

TABLE III
Influence of Monomers' Mole Ratio to Copolymer
Inherent Viscosity

Monomers' mole ratio (DM/AT)	20	15	10	2
Inherent viscosity	33.842	72.122	81.611	97.8626

: 1 (mole ratio) controlled the reaction temperature at 80–90°C (the power ~ 10–15 mA), the polymer yield increased with the increasing of reaction time. However, when reaction time improved to about 8 h, the conversion reached the maximum and fixed value, because with reaction time increasing, the system viscosity increased along with the monomer conversion, which limited the radical's movement, and even embedded the radical when the monomer conversion was difficult to raise anymore.

Influence of microwave irradiation power to the inherent viscosity of polymer. As shown in Table I, the monomer conversion reached maximum when reaction time was 8 h. From Table II, when the microwave irradiation power improved to around 20 mA, the viscosity went down. It is due to the increase of radical number resulting from the increase of irradiation energy.

Influence of monomers' mole ratio to copolymer inherent viscosity. As shown in Table III, in the range of experiment, when DM : AT = 2 : 1, the inherent viscosity of copolymer was maximum; after that, along with the increasing the quantity of DM, the inherent viscosity of copolymer went down, and when DM : AT = 20 : 1, the inherent viscosity was least. It showed that the increasing of AT in the copolymer will result in the increasing of inherent viscosity.

IR spectrum

In the IR spectra of P(DM-*Co*-AT), there are V_{C-N} peak (1161.2 cm^{-1}) and $V_{C=S}$ peak (1064.8 cm^{-1}). The wide IR peak at 1111.1 cm^{-1} in IR of spectra of Cu-P(DM-*Co*-AT) should be the migration of the two peaks [V_{C-N} peak and $V_{C=S}$ peak in IR spectra of P(DM-*Co*-AT)] resulting from the N and S of the copolymer coordinated with the Cu^{2+} . Because the different groups and different chemical bonds present

TABLE V
Relationship between the Content of Na_2SO_3 and
 \bar{M}_w of PMMA

Content of Na_2SO_3 (%)	1.6	1.2	0.6	0.4	0.2
\bar{M}_w of PMMA (10^4)	47.3	40.6	142	142.8	86.1

feature IR absorption,²⁰ the change of the IR peak was the criterion of coordination of Cu(II) with N, S in the copolymer P(DM-*Co*-AT).

ESR of Cu-P(DM-*Co*-AT)

As shown in Figure 1, the electronic spin resonance (ESR) curve of the Cu-P(DM-*Co*-AT) appeared at $g = 2.362$ and $g = 2.097$; the copolymer itself has no ESR sign, and Cu^{2+} has a $g = 2.190$. Because the change of ESR sign position or change of g value is relative to the nature of chemical bond,²¹ this testing displayed that Cu^{2+} coordinated with P(DM-*Co*-AT) to form Cu-P(DM-*Co*-AT); that is to say, a new coordinate bond formed between Cu^{2+} and polymer.

*X-ray photoelectron spectroscopy (XPS) of Cu-P(DM-*Co*-AT).* XPS of Cu-P(DM-*Co*-AT) showed that all the elements of the PMC were inspected except H. The inner electron's bonding energy of relative atoms is shown in the center column in Table IV. These data indicated that coordination occurred between Cu^{2+} and atoms of polymer. After coordination, 2p3 electron's bonding energy of Cu(II) (937.50 eV) was less than the electron's bonding energy (948 eV),²² which occurred before coordination. After coordination, the electron's bonding energy of N1s (405.10 eV) was greater than the one (400.4 eV) not coordinated. The electron's bonding energy of S2p (171.40 eV) changed also. Based on this testing result and valence-bond theory,²³ it can be considered that Cu(II) accepted a lone electron pair of N and S on the chain element of the P(DM-*Co*-AT) molecule. During the coordination, electric charge transferred as $\text{N} \rightarrow \text{Cu}$ and $\text{S} \rightarrow \text{Cu}$. Due to the curl and intertwist of the copolymer chain, Cu^{2+} could not completely coordinate with N and S of poly (DM-*co*-AT); Cu(II) was in unsaturated coordination state and possessed a vacant site in the poly-

TABLE IV
XPS Data of Cu-P(DM-*Co*-AT)

Peak	Center	SF	PK area	FWHM	Tx. function	Normal area	[AT]%
Cu2p3	937.50	4.20	8330.406	3.000	0.2	18.92676	2.178
O 1s	534.60	0.66	22,061.518	2.800	0.1	242.24675	34.746
N 1s	405.10	0.42	1953.522	4.000	0.1	31.62575	4.536
C 1s	288.00	0.25	14,774.004	3.400	0.1	381.68585	54.746
S 2p	171.40	0.54	1989.287	2.100	0.1	22.71395	3.258

TABLE VI
Relationship between the Content of Cu-P(DM-Co-AT)
and \bar{M}_w of PMMA

Content of Cu-P(DM-AT) (%)	1.6	1.2	0.8	0.6	0.4
\bar{M}_w of PMMA (10^4)	14	40.6	48	69.1	57.8

meric complex, which might be the reason for PMC's high catalysis reactivity.

Cu-P(DM-Co-AT)/Na₂SO₃ initiated polymerization of vinyl monomer

The polymerization of MMA was examined at room temperature in the presence of water. It was found that the MMA could not polymerize when a random quantity of Na₂SO₃ or 5 ml Cu-P(DM-Co-AT) aqueous was added into 10 g MMA. However, when the two existed at the same time, they polymerized after about 3 min. It displayed that Cu-P(DM-Co-AT)/Na₂SO₃ aqueous was the initiator of MMA.

\bar{M}_w of PMMA obtained was determined by GPC. When the content of Cu-P(DM-Co-AT) was controlled as 1.2% of the weight of monomers, the content of Na₂SO₃ changed. Table V, shows that, when the content of Na₂SO₃ was 0.4–0.7% of the weight of monomers, the \bar{M}_w of the obtained PMMA was maximum, and the \bar{M}_w of PMMA decreased along with the increasing content of Na₂SO₃ and trended to a basically stable value. Because the Na₂SO₃ was the main source of primary radicals, when the content of Na₂SO₃ increased, the number of radical increased also, and it resulted in the decreasing of \bar{M}_w .

When the content of Na₂SO₃ was controlled as 1.2% of the weight of MMA, the content of Cu-P(DM-Co-AT) changed. Table VI displays that, when the content of the Cu-P(DM-Co-AT) was about 0.6% of monomer, the \bar{M}_w of obtained PMMA was maximum, and after 0.6%, the \bar{M}_w of PMMA decreased along with the increasing content of Cu-P(DM-Co-AT). Cu-P(DM-Co-AT) was the place that can accelerate the generation of radicals; increasing it will result in the decreasing of \bar{M}_w .

CONCLUSION

Copolymerization of DM and AT and the coordination of the copolymer with Cu(II) can be under microwave

irradiation. Cu-P(DM-Co-AT) was obtained. Cu-P(DM-Co-AT) has the function to catalyze the polymerization of MMA. The \bar{M}_w of PMMA obtained was high, to 1,400,000, far greater than that obtained by a traditional initiator. Furthermore, the catalytic system was a heterogeneous system, and the solid catalyst Cu-P(DM-Co-AT) was easy to be separated from the reactions system. It also supplied an effective way to prepare a high-purity heavy polymer.

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References

- Gedye, R. N.; Smith, F. E.; Westaway, K. *Tetrahedron Lett* 1986, 27, 279.
- Giguere, R. J.; Bray, T. L.; Duncan, S. M. *Tetrahedron Lett* 1986, 27, 4945.
- Teffal, M.; Gourdenne, A. *Eur Polym J* 1983, 19, 543.
- Stoffer, J. O.; Sitatram, S. P. *Am Chem Soc, Proc Polym Mater Sci Eng* 1994, 71, 55.
- Dori, A. D.; Huggett, R.; Bates, J. F. *Dent Mater* 1988, 4, 25.
- Mijovic, J.; and Wijaya, J. *Polym Compos* 1990, 11, 184.
- Thuillier, F. M.; Jullien, H.; Grenier-Loustalot, M. F. *Polym Commun* 1986, 27, 206.
- Lewis, D. A.; Hedrick, J. C.; McGrath, J. E.; Ward, T. C. *Am Chem Soc, Polym Prepr* 1987, 28(2), 330.
- Silinski, B.; Kuzmyca, C.; Gourdenne, A. *Eur Polym J* 1987, 2, 273.
- Jullien, H.; Valot, H. *Polymer* 1985, 26, 506.
- Silinski, B.; Kuzmycz, C.; Groudene, A. *Eur Polym J* 1987, 23, 273.
- Kishanprasad, V. S.; Gedam, P. H. *J Appl Polym Sci* 1993, 50, 419.
- Lu, J. M.; Zhu, X. L. *J Appl Polym Sci* 1998, 68, 1563.
- Lu, J. M.; Zhu, X. L. *J Appl Polym Sci* 1997, 66, 129.
- Lu, J. M.; Ji, S. J.; Wu, J. F.; Zhou, G. H.; Dai, W. Q.; Zhu, X. L. *J Macromol Sci, A* 2002, 39(4), 351.
- Lu, J. M.; Jiang, Q. S.; Zhu, X. L.; Wang, Fa. *J Appl Polym Sci* 2001, 79, 312.
- Lu, J. M.; Chen, N. Y.; Ji, S. J.; Sun, Z. R.; Ping, M. X.; Zhu, X. L. *J Appl Polym Sci* 2001, 82, 1356.
- Baghurst, D. R.; Cooper, S. R.; Greene, D. L. *Polyhedron* 1990, 9, 893.
- Michael, D.; Mingos, P. *J Chem Soc., Chem Commun* 1996, 899.
- Li, Q. L.; Chi, X. Z.; Zeng, Y. H. *Instrument Analysis*; Beijing Normal School Publishing Company: Beijing, 1990; p 184.
- Zeng, X. Y. *Introduction of Structure Analysis*; Science Publishing Company: Beijing, 1980; p 520.
- Boting, E. P. *Principle and Application of X-ray Spectrum Analysis*; National Defence Industry Publishing Company, America, 1983; p 537.
- Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Wiley: New York, 1972; p 492.