

Synthesis of Polyacrylonitrile via Reverse Atom Transfer Radical Polymerization Initiated by 1,1,2,2-Tetraphenyl-1,2-ethanediol/FeCl₃/Triphenylphosphine

Chen Hou,¹ Liang Ying²

¹College of Chemistry and Materials Science, Yantai Normal University, Yantai 264025, China

²Office of Science and Technology, Yantai Normal University, Yantai 264025, China

Received 22 July 2005; accepted 14 January 2006

DOI 10.1002/app.24167

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: FeCl₃ coordinated by triphenylphosphine was first used as the catalyst in the 1,1,2,2-tetraphenyl-1,2-ethanediol-initiated reverse atom transfer radical polymerization of acrylonitrile. A FeCl₃/triphenylphosphine ratio of 0.5 not only gave the best control of the molecular weight and its distribution but also provided a rather rapid reaction rate. The rate of polymerization increased with increasing polymerization temperature, and the apparent activation energy was calculated to be 62.4 kJ/mol. When FeCl₃ was replaced with CuCl₂, the reverse atom transfer radical poly-

merization of acrylonitrile did not show prominent living characteristics. To demonstrate the active nature of the polymer chain end, the polymers were used as macroinitiators to advance the chain-extension polymerization in the presence of a CuCl/2,2'-bipyridine catalyst system via a conventional atom transfer radical polymerization process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 4041–4045, 2007

Key words: atom transfer radical polymerization (ATRP); living polymerization; kinetics (polym.)

INTRODUCTION

A narrow polydispersity is an essential requirement for the synthesis of polyacrylonitrile (PAN) polymers satisfying the requirements for high-performance PAN fibers.^{1,2} PAN is usually prepared by radical polymerization without control over the molecular dimensions and structure, whereas other methods exist for more controlled polymerizations of acrylonitrile (AN), such as anionic polymerization, which often involves complex catalysis or side reactions with the nitrile groups.³ Living/controlled free-radical polymerization can be used as an alternative; atom transfer radical polymerization (ATRP) is one of the most widely used methods, involving a fast, dynamic equilibrium between dormant species and active radical species to provide control.^{4–9} However, transition-metal-catalyzed ATRP has a major drawback: the oxidation of the catalyst by oxygen in air. To overcome this drawback, the use of conventional radical initia-

tors in the presence of complexes of transition metals in their higher oxidation state has been reported as reverse or alternative ATRP by Matyjaszewski and coworkers.^{10,11} So far, two types of efficient reverse ATRP initiating systems for living/controlled radical polymerization have been reported, that is, azobisisobutyronitrile (AIBN)/CuCl₂ (or CuBr₂)/2,2'-bipyridine (bipy) for methyl methacrylate (MMA), methyl acrylate, and styrene polymerization and AIBN/FeCl₃/triphenylphosphine (PPh₃) for MMA polymerization.¹² Braun and Becker^{13,14} reported that 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED) could be used as an initiator for the common radical polymerization and copolymerization of vinyl monomers. In this study, a new initiating system based on TPED with FeCl₃/PPh₃ as a catalyst was first used in the reverse ATRP of AN. The effects of the ratio of the metal to the ligand were investigated. The influences of the different transition metals on reverse ATRP were also investigated.

EXPERIMENTAL

Materials

Analytical-reagent-grade AN (Shanghai Chemical Reagents Co., Shanghai, China) was vacuum-distilled from CaH₂ just before polymerization. Analytical-reagent-grade FeCl₃ (Shanghai Chemical Reagents) was washed with absolute ethanol and dried *in vacuo* at 60°C before use. TPED was used as an initiator and prepared from benzophenone and 2-propanol according to the literature.¹⁵ PPh₃ (Aldrich, Milwaukee, WI)

Correspondence to: C. Hou (sdchenhou@hotmail.com).

Contract grant sponsor: Youth Science Foundation, Department of Science and Technology, Shandong Province; contract grant number: 2005BS11010.

Contract grant sponsor: Natural Science Foundation, Department of Science and Technology, Shandong Province; contract grant numbers: Q2006F05, Y2005F11.

Contract grant sponsor: Natural Science Foundation, Ludong University; contract grant numbers: L20062901, 032912, 20052901.

Journal of Applied Polymer Science, Vol. 104, 4041–4045 (2007)
© 2007 Wiley Periodicals, Inc.

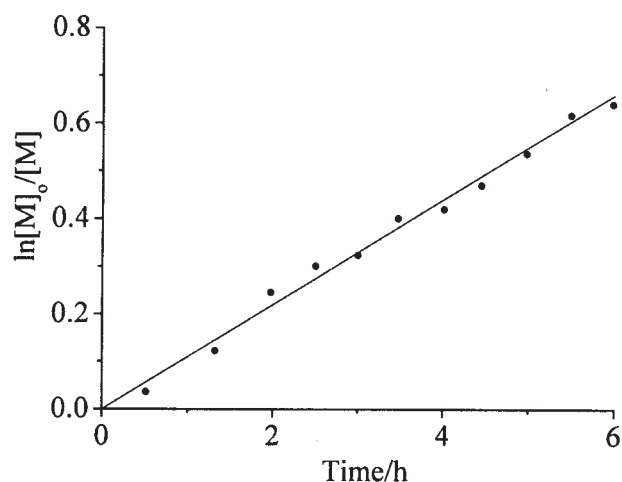


Figure 1 First-order kinetic plot of the monomer consumption as a function of time during the reverse ATRP of AN ([AN] = 6.0M, [AN]/[TPED]/[FeCl₃]/[PPh₃] = 400 : 1 : 1 : 2, temperature = 70°C).

was prepared by recrystallization from ethanol to eliminate triphenylphosphine oxide. *N,N*-Dimethylformamide (DMF; Shanghai Dongyi Chemical Reagents Co., Shanghai, China) was distilled under reduced pressure and stored over 4-Å molecular sieves before use. Analytical-reagent-grade CuCl (Shanghai Chemical Reagents) was used as received.

Polymerization

A typical example of the general procedure was as follows. A dry flask was filled with FeCl₃, PPh₃, TPED, and AN in that order. It was degassed *in vacuo* and charged with N₂ (four times) and was sealed under N₂. The flask was then immersed in an oil bath held at the desired temperature by a thermostat. After a definite time, the polymerization was terminated by the cooling of the flask in ice water. The polymerization product was dissolved in DMF. The resultant mixture was then poured into a large amount of methanol for precipitation, washed with methanol several times, and dried at 60°C *in vacuo*.

Characterization

The conversion of the monomer was determined gravimetrically. The number-average molecular weight (M_n) and polydispersity index (PDI) of the AN polymers were measured by gel permeation chromatography (GPC). GPC was performed with a Waters (Milford, MA) model 515 solvent delivery system at a flow rate of 1.0 mL/min through a combination of Waters HR1, HR3, and HR4 Styragel columns. Poly(methyl methacrylate) standards were used to calibrate the columns. The analysis was undertaken at 30°C with purified, high-performance-liquid-chromatography-grade DMF as an eluent. A

Waters model 2410 differential refractometer was used as the detector.

For comparison with the aforementioned measurements of M_n , the viscosity-average molecular weight (\overline{M}_η) of the AN polymers was determined with intrinsic viscosity ($[\eta]$) measurements. $[\eta]$ of the AN polymers was measured at 30°C in DMF with an Ubbelohde viscometer (Shanghai Bao Shan Qi Hang Glass Instrument Factory, Shanghai, China),¹⁶ and the molecular weight was calculated with the following equation:

$$[\eta] = 3.92 \times 10^{-4} \overline{M}_\eta^{0.75} \quad (1)$$

RESULTS AND DISCUSSION

Polymerization of AN with the TPED/FeCl₃/PPh₃ initiating system

AN was polymerized with FeCl₃/PPh₃ as the catalyst and TPED as the initiator at 70°C ([AN]/[TPED]/[FeCl₃]/[PPh₃] = 400 : 1 : 1 : 2). After heating, a change in color from light brown was observed. This corresponded to the decomposition of TPED and the establishment of the equilibrium between Fe³⁺ and Fe²⁺. Figure 1 shows kinetic plots of ln [M]₀/[M] versus time (where [M]₀ is the initial monomer concentration and [M] is the monomer concentration). The linearity of the plot indicates that the polymerization is approximately first-order with respect to the monomer concentration. The slope of the kinetic plots indicates that in the polymerization process, the number of active species is constant, and the termination reactions can be neglected. The monomer conversion reached about 48.3% within 6 h. The corresponding value of the apparent rate constant (k_p^{app}), calculated from the kinetic plot, was $3.06 \times 10^{-5} \text{ s}^{-1}$.

Figure 2 presents M_n and \overline{M}_η of the resulting polymers, which increase linearly with the conversion.

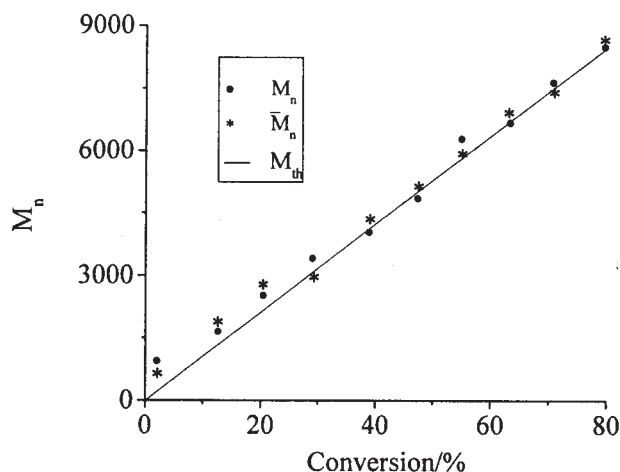
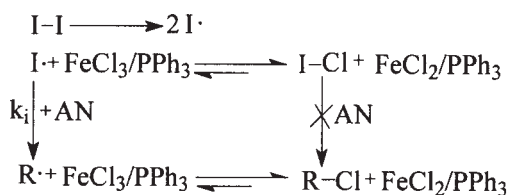
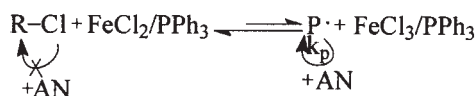


Figure 2 Dependence of M_n on the monomer conversion for the reverse ATRP of AN ([AN] = 6.0M, [AN]/[TPED]/[FeCl₃]/[PPh₃] = 400 : 1 : 1 : 2, temperature = 70°C).

Initiation:**Propagation:**

Scheme 1 Polymerization mechanism of the reverse ATRP of AN, including the ligand structure (k_i = initiation constant, k_p = propagation constant).

The high molecular weight at a conversion less than 20% indicates that there might have been too many primary radicals produced from the decomposition of TPED at the beginning of the reaction, which could not become the dormant species by halogen transfer and undergo termination by combination reactions. A similar phenomenon has been observed previously.¹⁷ The values of \overline{M}_n determined by GPC agreed well with those of \overline{M}_n determined by $[\eta]$. Both M_n and \overline{M}_n agreed reasonably well with the theoretical molecular weight (M_{th}). These results reveal that the polymerization of AN with the TPED/FeCl₃/PPh₃ initiating system is a living/controlled radical polymerization process. A polymerization mechanism is proposed, as described in Scheme 1. In the initiation step, after the homolytic decomposition of one TPED (I—I) into two primary radicals (I·), these radicals can add to the monomer.

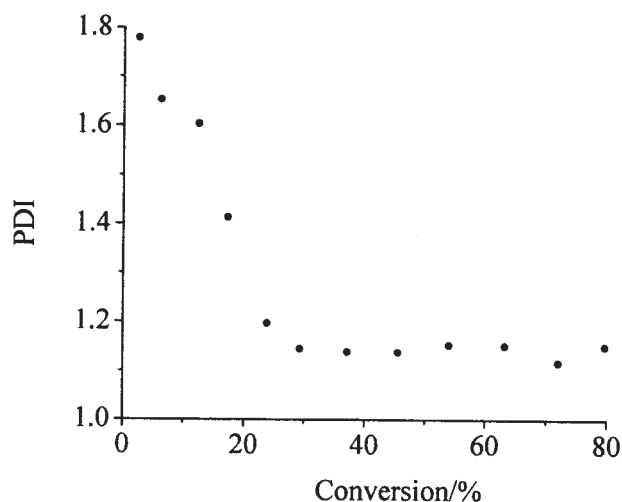


Figure 3 Dependence of PDI on the monomer conversion for the reverse ATRP of AN ($[\text{AN}] = 6.0\text{M}$, $[\text{AN}]/[\text{TPED}]/[\text{FeCl}_3]/[\text{PPh}_3] = 400 : 1 : 1 : 2$, temperature = 70°C).

TABLE I
Data for the Reverse ATRP of AN Catalyzed by FeCl₃/PPh₃

[FeCl ₃]/[PPh ₃]	Time (h)	Conversion (%)	M_{th}	M_n	\overline{M}_n	PDI	$k_p^{app} \times 10^5$ (S ⁻¹)
1 : 1	6	32.3	3424	3680	3750	1.23	1.81
1 : 2		48.3	5120	5240	5320	1.16	3.06
1 : 4		41.5	4399	4650	4720	1.25	2.48
1 : 6		39.8	4219	4340	4410	1.31	2.35

$[\text{AN}] = 6.0\text{M}$; $[\text{AN}]/[\text{TPED}]/[\text{FeCl}_3] = 400 : 1 : 1$; temperature = 70°C.

Then, the activated monomer radicals (R·) react with FeCl₃/PPh₃ through chlorine atom transfer and generate the lower oxidation state metal complex (FeCl₂/PPh₃). Finally, the polymer propagates via a conventional ATRP process.

The PDI values of the AN polymers are shown in Figure 3. The polydispersity was narrow (PDI = 1.16) when the conversion ranged from 20 to 50%. A broader polydispersity was obtained when the conversion was less than 20%. This suggests that conventional radical polymerization takes place during the initial polymerization in the reaction system. In other words, the reverse ATRP system will set up as the conversion goes beyond 20%.

Effect of PPh₃ on the reverse ATRP of AN

It has been reported that PPh₃ might reduce the initiator efficiency, leading to an increase in the observed molecular weight. To further investigate the effects of PPh₃, a series of experiments with the reverse ATRP of AN were carried out in the presence of a large amount of the ligand. The results have been compiled in Table I. In this study, different conclusions were drawn: the monomer conversion reached about 32.3%, 48.3, and 41.5% with 1 : 1, 1 : 2, and 1 : 4 [FeCl₃]/[PPh₃] ratios, respectively, within 6 h. Comparing the k_p^{app} values derived from the kinetic plots, we found that the reaction rate corresponding to the ratio of 1 : 2 was the highest one. Lower or higher concentrations of PPh₃ resulted in a low reaction rate. This illustrates that a large amount of PPh₃ not only poisons the metal catalyst but also has a role in producing a more significant

TABLE II
Kinetic Data for the Reverse ATRP of AN at Different Temperatures in DMF

Temperature (°C)	$k_p^{app} \times 10^5$ (S ⁻¹)	Temperature (°C)	$k_p^{app} \times 10^5$ (S ⁻¹)
65	2.19	72	3.46
70	3.06	75	4.17

$[\text{AN}] = 6.0\text{M}$; $[\text{AN}]/[\text{TPED}]/[\text{FeCl}_3]/[\text{PPh}_3] = 400 : 1 : 1 : 2$.

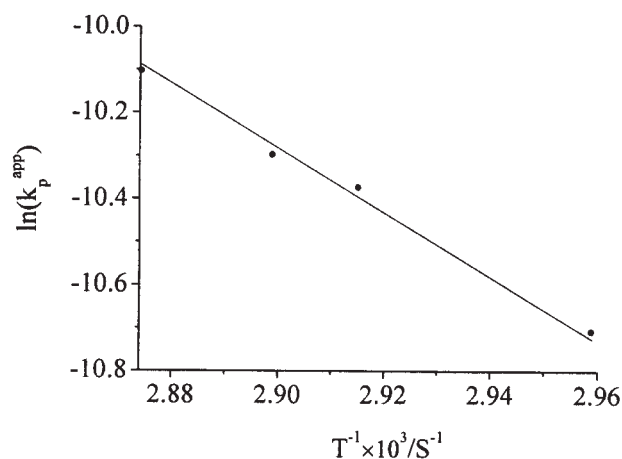


Figure 4 Effect of the temperature (T) on k_p^{app} .

side reaction, such as a reaction with active species, or catalyzing the elimination of the initiator.

Effect of the polymerization temperature on the polymerization

The effect of the polymerization temperature on the reverse ATRP of AN was investigated. The experimental results are given in Table II. k_p^{app} increases with increasing temperature. An Arrhenius plot obtained from the experimental data given in Table II is given in Figure 4. The apparent activation energy was calculated to be 62.4 kJ/mol.

Effects of the different transition-metal ions

The effects of different transition metals on reverse ATRP were investigated in the polymerization of AN with $[\text{AN}] = 6.0\text{M}$ and $[\text{AN}]/[\text{TPED}]/[\text{CuCl}_2]/[\text{PPh}_3] = 400 : 1 : 1 : 2$ at 70°C . Table III shows the outcomes for the polymerization of AN with $\text{CuCl}_2/\text{PPh}_3$ as the catalyst system. The molecular weight increased with the monomer conversion, which showed somewhat living characteristics. However, the measured molecular weight was much higher than the calculated values, and the molecular weight distribution was rather wide. The living species seemed rather active, and this led to radical-radical termination.

TABLE III
Data for the Reverse ATRP of AN Catalyzed by $\text{CuCl}_2/\text{PPh}_3$

Time (h)	Conversion (%)	M_{th}	M_n	\bar{M}_n	PDI
1	8.61	911	66,750	68,760	1.84
2	17.8	1,887	76,260	77,850	1.79
4	34.3	3,636	89,450	90,340	1.26
6	45.7	4,844	101,260	104,570	1.31

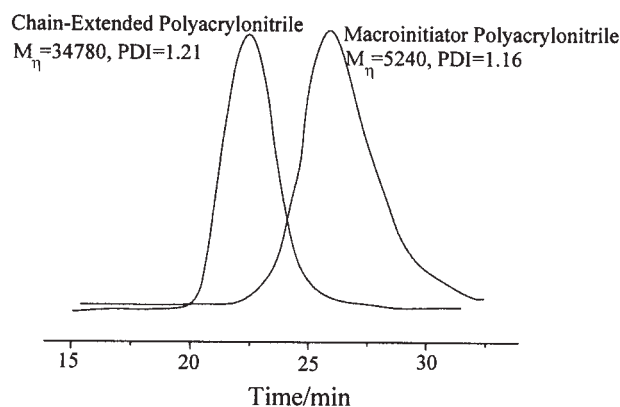


Figure 5 GPC curves of PAN before and after a chain-extension reaction.

Chain extension of PAN

An additional method for verifying the functionality of a polymer prepared by reverse ATRP is its use as a macroinitiator for the same or other monomers.¹⁸ The extension polymerization of PAN ($M_n = 5240$, $\text{PDI} = 1.16$) with AN was carried out in bulk at 90°C in the presence of the $\text{CuCl}_2/\text{bipy}$ catalyst system. As shown in Figure 5, when $[\text{AN}]$ was 7.0M , $[\text{AN}]/[\text{PAN}]/[\text{CuCl}_2]/[\text{bipy}]$ was $500 : 1 : 1 : 2$, and the time was 25 h, the conversion was greater than 95%. The PAN obtained had $M_n = 34,780$ and $\text{PDI} = 1.21$. This clearly demonstrated that the chain extension of PAN took place. However, the molecular weight distribution (1.21) was a little broader than that of the macroinitiator (1.16) because some of the macroinitiator probably was not active. The chain-extension polymerization of the obtained PAN verifies the active nature of the precursor chain end.

CONCLUSIONS

A new catalyst system, $\text{FeCl}_3/\text{PPh}_3$, was successfully used in the reverse ATRP of AN. Well-defined PAN was synthesized. When the ratio of FeCl_3 to PPh_3 was 0.5, the polymerization was best controlled. The rate of polymerization increased with increasing polymerization temperature, and the apparent activation energy was calculated to be 62.4 kJ/mol. When FeCl_3 was replaced with CuCl_2 , the measured molecular weight was much higher than the calculated values, and the molecular weight distribution was rather wide. The obtained PAN could act as a macroinitiator for extension polymerization.

References

- James, C. M. *Acrylic Fiber Technology and Application*; Marcel Dekker: New York, 1995.
- Chen, H.; Wang, C.; Liang, Y.; Cai, H. *Chin J Chem Eng* 2003, 11, 166.

3. Ono, H.; Hisatani, K.; Kamide, K. *Polym J* 1993, 25, 245.
4. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
5. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
6. Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
7. Smith, Q.; Huang, J.; Matyjaszewski, K.; Loo, Y. L. *Macromolecules* 2005, 38, 5581.
8. Pintauer, T.; Braunecker, W.; Collange, E.; Poli, R.; Matyjaszewski, K. *Macromolecules* 2004, 37, 2679.
9. Brar, A. S.; Saini, T. *J Polym Sci Part A: Polym Chem* 2005, 43, 2810.
10. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7572.
11. Xia, J.; Matyjaszewski, K. *Macromolecules* 1997, 30, 7692.
12. Moineau, G.; Dubois, P.; Jerome, R.; Senninger, T.; Teyssie, P. *Macromolecules* 1998, 31, 545.
13. Braun, D.; Becker, K. H. *Ind Eng Chem Prod Res Dev* 1971, 10, 386.
14. Braun, D.; Becker, K. H. *Angew Makromol Chem* 1969, 6, 186.
15. Chen, X. P.; Qiu, K. Y. *J Appl Polym Sci* 2000, 67, 1607.
16. Kashyap, A. K.; Kalpagam, V. *J Polym Sci: Polym Chem Edit* 1979, 17, 225.
17. Chen, X.; Qiu, K. *Macromolecules* 1999, 32, 8711.
18. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7572.