Synthesis of Polyacrylonitrile via Reverse ATRP Initiated by 1,1,2,2-Tetraphenyl-1,2-Ethanediol/CuCl₂/2,2'-Bipyridine

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ABSTRACT: The reverse atom-transfer radical polymerization (RATRP) technique using $CuCl_2$/2,2'-bipyridine (bipy) complex as a catalyst was applied to the living-radical polymerization of acrylonitrile (AN). 1,1,2,2-Tetraphenyl-1,2-ethanediol (TPED) was first used as the initiator in this copper-based RATRP initiation system. A $CuCl_2$ to bipy ratio of 0.5 not only gives the best control of molecular weight and its distribution, but also provides rather rapid reaction rate. The rate of polymerization increases with increasing the polymerization temperature, and the apparent activation energy was calculated to be 53.2 kJ mol^{-1}. Because the polymers obtained were end-functionalized by chlorine atoms, they were used as macroinitiators to proceed the chain extension polymerization in the presence of CuCl/bipy catalyst system via a conventional ATRP process. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3529–3533, 2007

Key words: reverse atom transfer radical polymerization; living polymerization; acrylonitrile

INTRODUCTION

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 molecular dimension and structure, while other methods exist for more controlled polymerization 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, which involves a fast dynamic equilibrium between dormant species and active radical species to provide control.[4–6] However, transition-metal-catalyzed ATRP has two major drawbacks: the toxicity of the halide species RX and the oxidation of the catalyst M_n^t/LX by oxygen in air. To overcome these drawbacks, the use of conventional radical initiators in the presence of complexes of transition metals in their higher oxidation state have been reported and referred to as reverse ATRP (RATRP) by Matyjaszewski and coworkers.[7,8] In the past, only two kinds of initiators, such as azo- and peroxide compounds, were employed as the initiator in the RATRP system. It is well-known that the decomposition of conventional initiators is irreversible, which makes the concentration of primary radicals rather high, especially at the early stage of polymerization at high temperature. The development of new type initiators for RATRP, using carbon–carbon bond initiator, instead of azo or peroxide ones, is of interest. This new type initiator (an iniferter) could provide the initiation step of RATRP, in which the iniferter reversibly decomposes to primary radicals, unlike other conventional initiators resulting in suitable amounts of primary radicals being generated. Chen has introduced a new initiating system 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED), instead of AIBN, into the iron-based RATRP system for styrene polymerization.[9] In this study, the living polymerization of AN with a new copper-based RATRP process, by using a TPED/$CuCl_2$/bipy initiation system, was first described. Effects of the ratio of metal to ligand were investigated. Effects of temperature on the polymerization were also discussed.

EXPERIMENTAL

Materials

Acrylonitrile (AN, Shanghai Chemical Reagents, A. R. grade) was vacuum distilled from CaH_2 just before polymerization. $CuCl_2$ (anhydrous) was prepared

from $CuCl_2 \cdot 2H_2O$ (Shanghai Chemical Reagents, A. R. grade) treated with thionyl chloride according to reference procedure[10] and dried under vacuum at 60°C before use. TPED was used as an initiator and prepared from benzophenone and 2-propanol. 2,2'-bipyridine (bipy, Shanghai Chemical Reagents, A. R. grade) was recrystallized from acetone. N,N-dimethylformamide (DMF, Shanghai Dongyi Chemical Reagents) was distilled at reduced pressure and stored over type4-Å molecular sieves before use.

Polymerization

A typical example of the general procedure was as follows. A dry flask was filled with $CuCl_2$, bipy, TPED, and AN in that order. It was degassed in vacuum and charged with N_2 (four times) and was sealed under N_2. The mixture was stirred at room temperature until the catalyst was dissolved. 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 cooling 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 under vacuum.

Characterization

The conversion of the monomer was determined gravimetrically. The molecular weight (M_n) and polydispersity index (PDI) of AN polymers were measured by gel-permeation chromatography (GPC). GPC was performed with a Waters model 515 solvent delivery system (Milford, MA) at a flow rate of 1.0 mL min^{-1} through a combination of Waters HR1, HR3, and HR4 styragel columns. Polystyrene strands 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.

The molecular weight ($\bar{M}_n$) of AN polymers was determined by the intrinsic viscosity measurements. The intrinsic viscosity [η] of AN polymers was measured at 30°C in DMF using an Ubbelohde viscometer,[11] and the molecular weight was calculated from the following equation.

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_n^{0.75} \qquad (1)$$

To compare with the above measurements of the molecular weight of AN polymers, the theoretical molec-
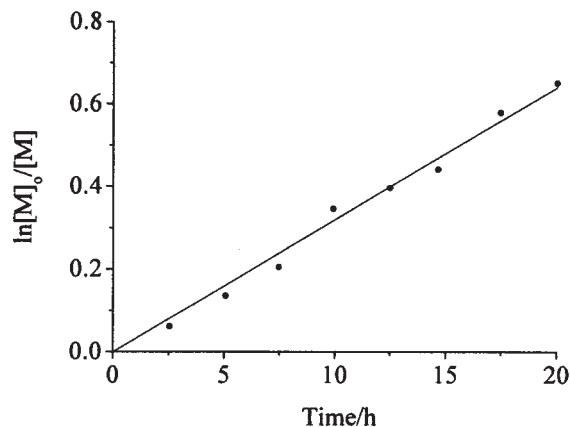
Figure 1 First-order kinetic plot of monomer consumption as a function of time during RATRP of AN with [AN] = 6.0M and [AN]:[TPED]:[$CuCl_2$]:[bipy] = 400:1:1:2 at 70°C.

ular weight (M_{th}) was used. According to the characteristics of living polymerization, M_{th} could be calculated from the following equation.[12]

$$M_{th} = \frac{[AN]}{2[DCDTS]} \times M_{wAN} \times Conversion \qquad (2)$$

where $M_{w\ AN}$ is the molecular weight of AN.

RESULTS AND DISCUSSION

Polymerization of an with the TPED/CuCl₂/bipy initiating system

AN was polymerized catalyzed by $CuCl_2$/bipy with TPED as the initiator at 70°C ([AN]:[TPED]:[$CuCl_2$]: [bipy] = 400:1:1:2). After heating, a change of color from light brown to tint was observed. This corresponds to the decomposition of TPED and the establishment of the equilibrium between Cu^{2+} and Cu^+. Figure 1 shows kinetic plots of $ln[M]_0/[M]$ versus time. 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 47.3% within 20 h. The corresponding value of the apparent rate constant (k_p^{app}) calculated from the kinetic plot is 8.89×10^{-6} s^{-1}.

Figure 2 represents M_n and $\bar{M}_n$ of the resulting polymers increases linearly with conversion. The high-molecular weight at conversion less than 10% indicates there might have been too many primary radicals produced from the decomposition of TPED at the beginning of the reaction, which could not become dormant species by halogen transfer and undergo termination by combination reactions. A similar phe-
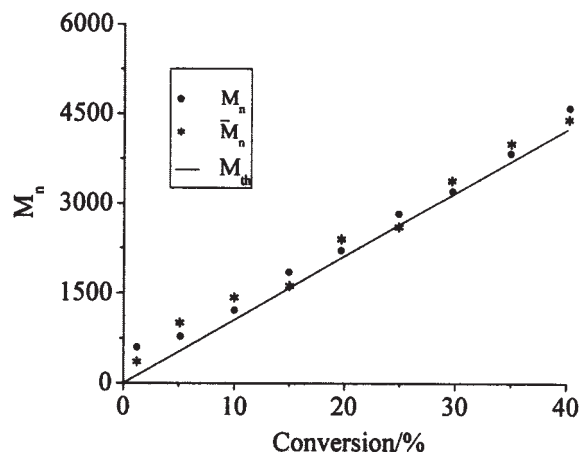
Figure 2 Dependence of M_n on the monomer conversion for RATRP of AN with [AN] = 6.0M and [AN] : [TPED] : [CuCl$_2$] : [bipy] = 400 : 1 : 1 : 2 at 70°C.

Figure 3 Dependence of PDI on the monomer conversion for RATRP of AN with [AN] = 6.0M and [AN] : [TPED] : [CuCl$_2$] : [bipy] = 400 : 1 : 1 : 2 at 70°C.

nomenon has been observed.[13] The values of M_n determined by GPC agree well with those of $\bar{M}_n$ determined by the intrinsic viscosity. Both M_n and $\bar{M}_n$ agree reasonably well with the theoretical molecular weight (M_{th}). These results reveal that the polymerization of AN with TPED/CuCl$_2$/bipy initiating system is a living/controlled radical polymerization process. According to the literature reported,[14] the 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. Then, the
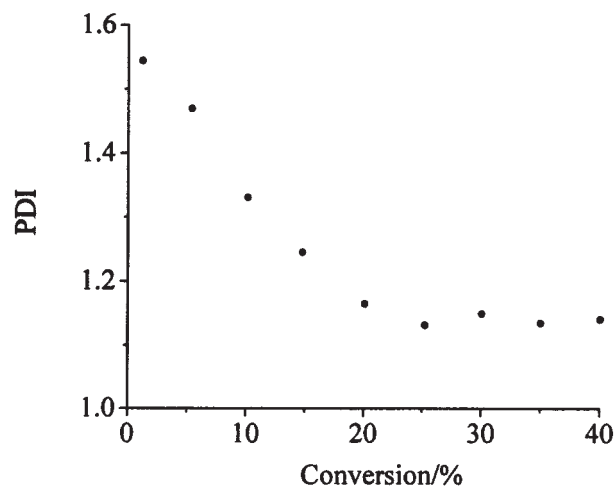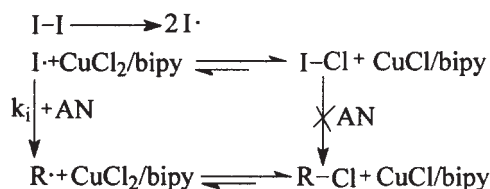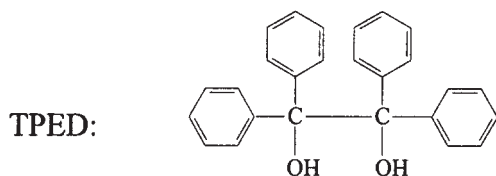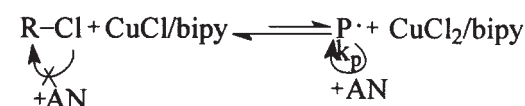
activated monomer radicals (R·) react with CuCl$_2$/bipy through chlorine atom transfer and generate the lower oxidation state metal complex, CuCl/bipy. Finally, the polymer propagates via a conventional ATRP process.

The values of PDI of AN polymers are shown in Figure 3. The polydispersity are narrow (PDI = 1.17) when the conversion is from 20 to 40%. A broader PDI is obtained when the conversion is less than 20%. This suggests that the conventional radical polymerization takes place during the initial polymerization in the reaction system. In other words, the RATRP system will set up as the conversion goes beyond 20%.

Effect of CuCl$_2$/bipy catalyst system on RATRP of AN

It has been reported that bipy might have decreased the initiator efficiency, leading to an increase in the observed molecular weight.[15] To further investigate the effects of bipy, a series of experiments of RATRP of AN were carried out. The results have been compiled in Table I. In this study, different conclusions are drawn. As more CuCl$_2$/bipy catalyst system was added (entries 1, 2, 3, 4), slower polymerization rates and narrower molecular weight distributions were observed, and the initiation efficiency f (calculated from $f = M_{th}/M_n$) also increased from 0.92 to 0.95, which suggests that the concentration of CuCl$_2$/bipy has a favorable influence on the activation as well as equilibrium of RATRP. With increasing the amount of bipy in the catalyst system (entries 1, 5, 6, 7), the rate of polymerization and initiation efficiency showed a trend of decrease while the molecular weight distribution of polymers remained narrow. This illustrates that a large amount of bipy not only poison the metal

Initiation:

$$I-I \longrightarrow 2\,I\cdot$$

$$I\cdot + CuCl_2/bipy \rightleftharpoons I-Cl + CuCl/bipy$$

$$k_i \downarrow +AN \qquad\qquad \times AN$$

$$R\cdot + CuCl_2/bipy \rightleftharpoons R-Cl + CuCl/bipy$$

Propagation:

$$R-Cl + CuCl/bipy \rightleftharpoons P\cdot + CuCl_2/bipy$$

$$\times \atop +AN \qquad\qquad k_p \atop +AN$$

TPED:

Scheme 1 Polymerization mechanism of RATRP of AN including the initiator structure.

TABLE I
Data for RATRP of AN Catalyzed by CuCl₂/bipy

Entry	[TPED]:[CuCl₂]:[bipy]	Time (h)	Conversion (%)	M_{th}	M_n	$\bar{M}_n$	PDI	k_p^{app} $(10^6/s^{-1})$	Initiation efficiency
1	1:1:2	20	47.3	5,014	5,450	5,380	1.17	8.89	0.92
2	1:2:4		42.1	4,463	4,800	4,910	1.15	7.59	0.93
3	1:3:6		36.8	3,901	4,150	4,200	1.14	6.37	0.94
4	1:4:8		31.4	3,328	3,500	3,480	1.12	5.23	0.95
5	1:1:1		51.5	5,459	5,810	5,850	1.16	10.1	0.94
6	1:1:4		40.1	4,251	4,780	4,820	1.18	7.12	0.89
7	1:1:6		35.6	3,774	4,340	4,320	1.17	6.11	0.87

[AN]=6.0M, [AN] : [TPED]=400 : 1, T = 70°C.

catalyst, but also it has a role in producing a more significant side reaction, such as a reaction with active species, or catalyzing the elimination of the initiator.

Effect of the polymerization temperature on the polymerization

Effect of the polymerization temperature on RATRP of AN was investigated. The experimental results are given in Table II. The apparent rate constant increases with increasing temperature. The Arrhenius plot obtained from the experimental data given in Table II was given in Figure 4. The apparent activation energy was calculated to be 53.2 kJ mol⁻¹. According to eq. (2) and ΔH_{prop} = 22.3 kJ mol⁻¹.[16]

$$\Delta H^0_{eq} = \Delta H_{app} - \Delta H_{prop} \qquad (3)$$

where ΔH^0_{eq} is the enthalpy of the equilibrium, ΔH_{app} is the apparent enthalpy of activation, and ΔH_{prop} is the activation enthalpy of propagation. Then, ΔH^0_{eq} = 30.9 kJ mol⁻¹ was calculated for RATRP of AN initiated by TPED/CuCl₂/bipy. This value is smaller than those for the polymerization of methyl methacrylate (ΔH^0_{eq} = 43.9 kJ mol⁻¹) for the FeCl₃/isophthalic acid system and is bigger than those for the polymerization of styrene (ΔH^0_{eq} = 26.5 kJ mol⁻¹) for the Cl-mediated system and 20.2 kJ mol⁻¹ for the Br-mediated system.

TABLE II
Kinetic Data for RATRP of AN at Different Temperature
with [AN]=6.0M and [AN] : [TPED] : [CuCl₂] : [bipy]
= 400 : 1 : 1 : 2

Temperature (°C)	k_p^{app} $(10^6/s^{-1})$
65	6.71
70	8.89
72	9.85
75	11.6

Chain extension of polyacrylonitrile

According to the initiation mechanism of TPED[17] and the mechanism polymerization of RATRP using TPED/CuCl₂/bipy system, the well-defined PAN with an ω-chlorine atom end groups will be obtained in the polymerization of AN using TPED/CuCl₂/bipy system. Therefore, the obtained PAN can act as a macroinitiator for the extension polymerization. The extension polymerization of the obtained PAN (M_n = 5450, PDI = 1.17) with AN was carried out in bulk at 85°C in the presence of the CuCl/bipy catalyst system. When [AN] = 7.0M, [AN] : [PAN] : [CuCl] : [bipy] = 500 : 1 : 1 : 2, t = 30 h, the conversion was > 95%. The PAN obtained was with M_n = 31,200, PDI = 1.21. It clearly demonstrates the chain extension of PAN takes place.

CONCLUSIONS

The new catalyst system, TPED/CuCl₂/bipy, was successfully used in the RATRP of AN. When the ratio of [CuCl₂]:[bipy] equals 0.5, the polymerization was best controlled. The rate of polymerization increases with increasing the polymerization temperature, and the apparent activation energy was calculated to be 53.2 kJ
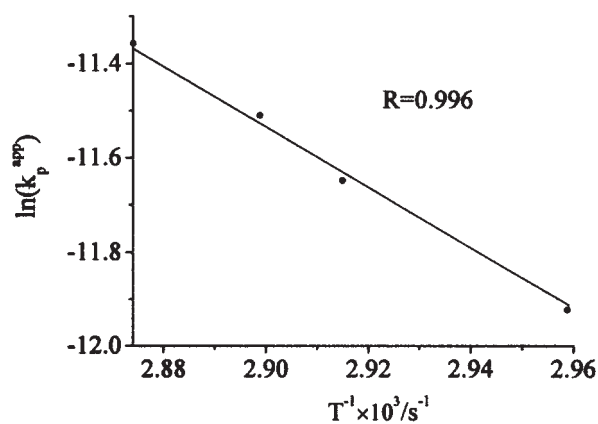

Figure 4 Effect of temperature on k_p^{app}.

mol^{-1}. PAN obtained were end-functionalized by chlorine atoms and can act as a macroinitiator for the extension polymerization.

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