Reverse ATRP of Methacrylonitrile with Diethyl 2,3-Dicyano-2,3-Diphenyl Succinate/SmCl$_3$/Lactic Acid

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Diethyl 2, 3-dicyano-2, 3-diphenyl succinate (DCDPS) was applied to initiate reverse atom transfer radical polymerization of methacrylonitrile (MAN) in *N*, *N*-dimethylformamide (DMF) with $SmCl_3$ and lactic acid (LA) as catalyst and ligand for the first time. The polymerization proceeded in a well-controlled manner as evidenced by kinetic studies. Compared with reverse atom transfer radical polymerization initiated by AIBN, the polymerization initiated by DCDPS not only showed better control of molecular weight, but also provided narrower molecular weight distribution. The slow polymerization rate and the broad polydispersity index were observed using cyclohexanone and toluene instead of DMF as reaction media. There was no apparent variation of the polymerization rate and polydispersity with initial monomer concentration. The block copolymer PMAN-b-PSt was obtained via a conventional ATRP process by using the resulting poly(methacrylonitrile) as macroinitiator.

Keywords: living polymerization, reverse atom transfer radical polymerization, methacrylonitrile

1 Introduction

Methacrylonitrile (MAN) is an interesting monomer. Poly(methacrylonitrile) (PMAN) is usually prepared by radical polymerization without control over molecular dimension and structure (1,2). Well-defined PMAN and their block copolymers have attracted much interest due to their potential applications (3). Living polymerization techniques could be employed to prepare well-defined polymers with predefined molecular weight, narrow molecular weight distribution and high degree of chain end functionalization (4,5). Living anionic and cationic polymerizations have been widely used in the preparation of a multitude of polymer materials. However, these techniques often suffer from several drawbacks, including the limited choice of monomers and solvents and high sensitivity to moisture and carbon dioxide (6,7). Living/controlled free radical polymerization can be used as an alternative. Atom transfer radical polymerization (ATRP) is one of the most powerful, versatile, simple and inexpensive methods in living/controlled free radical polymerization (8–17). However, transition metal catalyzed ATRP has two major drawbacks: toxicity of halide species RX and oxidation of catalyst M_n^t/LX by oxygen in air. To overcome these drawbacks, use of conventional radical initiators in the presence of complexes of transition metals in their higher oxidation state, has been reported and referred to as reverse ATRP by Matyjaszewski (18–20) and the other researchers (21). To the best of our knowledge, neither ATRP nor reverse ATRP of MAN has been approached.

It has been reported that in reverse ATRP, decomposition of conventional initiators, such as azo and peroxide compounds (22,23), is irreversible, which leads to the concentration of primary radicals rather high, especially at the early stage of polymerization at high temperature. Development of new type initiators for reverse ATRP is an essential requirement. The carbon-carbon bond thermal iniferter has been introduced as initiator for ATRP (24,25). Acids were generally believed to deactivate the metal organic catalyst, resulting in poor control of the polymerization. However, acids, which are inexpensive and nontoxic, complex more easily with samarium and may therefore, act as a ligand (26).

A detailed study for the optimization of the reaction conditions to prepare well-defined PMAN by reverse ATRP was the starting point of this original research. Keeping all these points in mind, a carbon-carbon bond thermal iniferter, diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS) was chosen to be the initiator, $SmCl_3$ and lactic acid (LA) were selected to be catalyst and ligand, and *N*, *N*-dimethylformamide (DMF) was used as the solvent. The successful approach of the well-controlled reverse ATRP of MAN was described for the first time. We found that this initiator and catalyst system could promote reverse ATRP of MAN with the desired characteristics of

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living/controlled radical polymerization. Effects of different initiators, catalyst system, initial monomer concentration and solvents on the polymerization were investigated. Block polymerization of styrene (St) via ATRP using PMAN as macroinitiator was also attempted.

2 Experimental

2.1 Materials

MAN (Xinhua Ruowei Chemical Co. Ltd., Hunan, China) were freed from inhibitor by washing with 5% NaOH and then with water several times. After drying over Na_2SO_4, they were distilled under reduced pressure. Anhydrous $SmCl_3$ (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China) was dried under vacuum before use. DCDPS was prepared according to the method reported previously (27). AIBN (AR grade, Tianjin Fuchen Chemical Reagents Factory) was recrystallized from ethanol and dried in a desiccator. DMF (AR grade, Tianjin Ruijinte Chemical Co. Ltd, Tianjin, China) was distilled at reduced pressure and stored over type4-Å molecurlar sieves before use. Lactic acid (AR grade, Tianjin Ruijinte Chemical Co. Ltd, Tianjin, China), cyclohexanone (AR grade, Tianjin Ruijinte Chemical Co. Ltd, Tianjin, China), and toluene (AR grade, Tianjin Ruijinte Chemical Co. Ltd, Tianjin, China) were used as received without further purification.

2.2 Polymerization

The general procedure was as follows. A dry flask was filled with the reagents in the order of DMF, LA, $SmCl_3$, DCDPS and MAN. It was degassed and charged with N_2 (three times). The mixture was sealed under N_2 and stirred at room temperature until the catalyst was dissolved. The flask was then immersed in an oil bath at the desired temperature detected by a thermostat, then followed by cooling in ice water after a definite time. The resultant mixture was then dissolved in DMF, and 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.

2.3 Characterization

The conversion of the monomer was determined gravimetrically.

The molecular weight (M_n) and polydispersity index (PDI) of PMAN were measured by gel permeation chromatography (GPC). GPC was performed with a Waters 1515 solvent delivery system (Milford, MA) at a flow rate of $1.0\,mL\cdot min^{-1}$ through a combination of Waters HT3, HT4, and HT5 styragel columns. Poly(methyl methacrylate) standards were used to calibrate the columns. The analysis was undertaken at 35°C with purified high-performance-liquid-chromatography-grade DMF as an eluent. A Waters 2414 differential refractometer was used as the detector.

According to the characteristics of living polymerization, the theoretical molecular weight (M_{th}) could be calculated from the following equation (28):

$$M_{th} = \frac{[MAN]}{2[DCDPS]} \times M_{wMAN} \times Conversion$$

where M_{WMAN} is the molecular weight of MAN.

3 Results and Discussion

3.1 Reverse ATRP of MAN initiated by DCDPS and AIBN

Reverse ATRP of MAN was carried out in DMF at 70°C with $SmCl_3$/LA as catalyst complex initiated by DCDPS and AIBN, respectively. Figure 1 shows the relationship between the monomer conversion and the reaction time. The monomer conversions increased with the reaction time, and the conversion initiated by AIBN was higher than by DCDPS. The monomer conversion initiated by AIBN reached 46.9% within 5 h, and the monomer conversion initiated by DCDPS reached 26.7%. Compared with reverse ATRP of MAN initiated by AIBN, about 20 min of induction period was required for reverse ATRP of MAN initiated by DCDPS. The induction period was perhaps caused by the thermal stability of DCDPS. DCDPS decomposed relatively slowly. During early stages of the polymerization, the primary radicals generated form DCDPS completely reacted with $SmCl_3$ to form the dormant species.

A plot of $\ln[M]_0/[M]$ vs. time is shown in Figure 2, the linearity of the plot indicated that the polymerization was approximately first-order with respect to the monomer concentration. It was suggested by the slope of the kinetic that the number of active species in the polymerization process was constant and the termination reactions could be
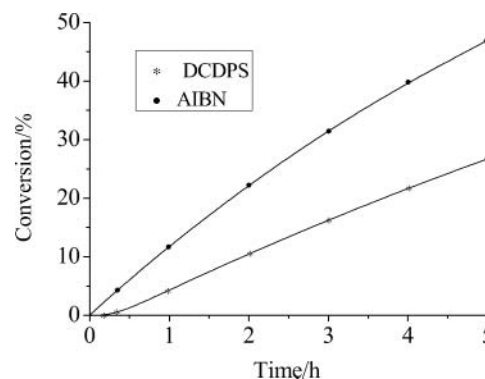

Fig. 1. Conversion dependence on the reaction time initiated by DCDPS and AIBN with [MAN] = 4.5 M and [MAN]:[Initiator]:[$SmCl_3$]:[LA] = 400:1:3:2 at 70°C.
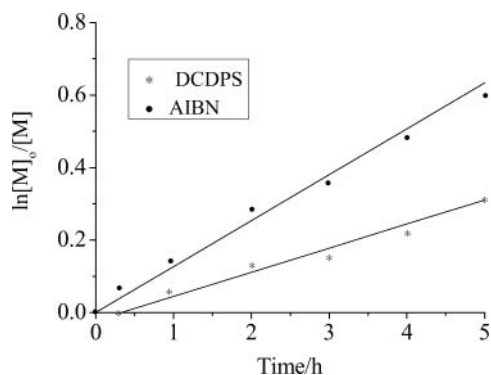
Fig. 2. Kinetics of reverse ATRP of MAN initiated by DCDPS and AIBN with [MAN] = 4.5 M and [MAN]:[Initiator]:[SmCl$_3$]:[LA] = 400:1:3:2 at 70°C.

neglected. According to the slopes of the kinetic plots, the apparent rate constant (k_p^{app}) of polymerization was calculated. The k_p^{app} (3.52×10^{-5} s^{-1}) initiated by AIBN was higher than by DCDPS (1.85×10^{-5} s^{-1}).

Figure 3 represents dependence of the molecular weight of the resulting PMAN vs. monomer conversion. As shown in Figure 3, M_n of the resulting PMAN initiated by both DCDPS and AIBN increased with conversion. In contrast with the resulting PMAN initiated by AIBN, M_n of the resulting PMAN initiated by DCDPS agreed better with those of the theoretical molecular weight (M_{th}) as conversion beyond 15%.

The values of PDI of the resulting PMAN initiated by both DCDPS and AIBN are shown in Figure 4. The polydispersity were narrower (PDI = 1.18) initiated by DCDPS than by AIBN (PDI = 1.25) when the conversion was in the range of 15 to 50%. A broader polydispersity was obtained when the conversion was less than 15%. The higher molecular weight and the broader PDI at conversion less than 15% suggested that there was some termination or side reaction at the beginning of the reaction because the radicals were not immediately deactivated.
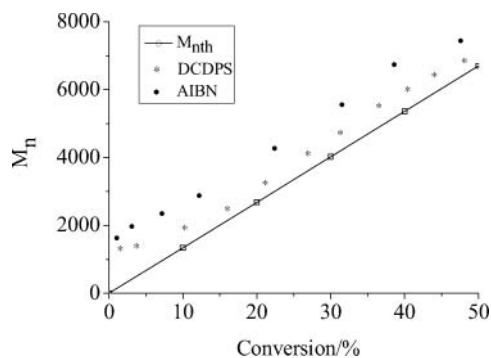

Fig. 4. Dependence of PDI on the monomer conversion for reverse ATRP of MAN initiated by DCDPS and AIBN with [MAN] = 4.5 M and [MAN]:[Initiator]:[SmCl$_3$]:[LA] = 400:1:3:2 at 70°C.

First-order kinetics of the polymerization rate with respect to the monomer concentration, linear increase of the molecular weight with monomer conversion and narrow polydispersity were indicative of living/controlled radical polymerization, which means that reverse ATRP of MAN with SmCl$_3$/LA as catalyst complex initiated by DCDPS was more controlled than by AIBN.

3.2 Effect of SmCl$_3$/LA Catalyst System on Reverse ATRP of MAN

In order to discuss effects of catalyst system on reverse ATRP of MAN initiated by DCDPS, a series of experiments were carried out. The results have been summarized in Table 1. When the ratio of [SmCl$_3$]/[LA] increased from 2:2 to 5:2 (entries 1, 2, 3, 4), slower polymerization rates and narrower molecular weight distributions were observed, which suggests that SmCl$_3$ itself was an effective catalyst in reverse ATRP. However, excess SmCl$_3$ would not only slow the polymerization rate significantly but also could contaminate the resultant polymers. With an increase amount of LA in the catalyst system (entries 2, 5, 6, 7), the rate of

Fig. 3. Dependence of M_n on the monomer conversion for reverse ATRP of MAN initiated by DCDPS and AIBN with [MAN] = 4.5 M and [MAN]:[Initiator]:[SmCl$_3$]:[LA] = 400:1:3:2 at 70°C.
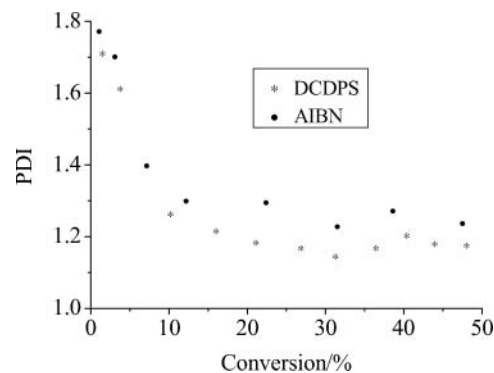
Table 1. Data for reverse ATRP of MAN initiated by DCDPS with [MAN] = 4.5 M and [MAN]:[DCDPS] = 400:1 at 70°C

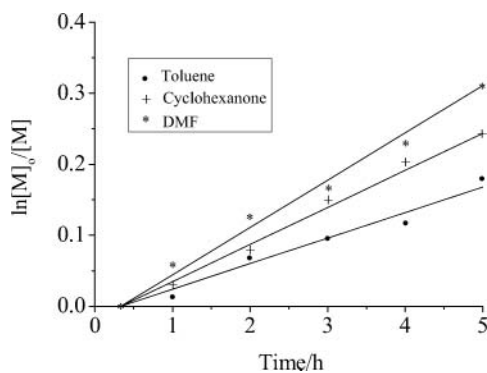| Entry	[DCDPS]: [SmCl$_3$]:[LA]	Reaction time/hour	Conversion/ %	M_{th}	M_n	PDI
1	1:2:2	5	32.1	4301	4420	1.23
2	1:3:2		28.3	3792	3950	1.18
3	1:4:2		26.4	3538	3690	1.17
4	1:5:2		25.1	3363	3570	1.15
5	1:3:1		34.6	4636	4910	1.17
6	1:3:3		25.7	3444	3650	1.18
7	1:3:4		23.4	3136	3350	1.19
8	1:1.5:1		30.8	4127	4320	1.25
9	1:6:4		26.7	3578	3780	1.16
10	1:9:6		24.1	3229	3490	1.14

Fig. 5. First-order kinetic plot of monomer consumption as a function of time in different solvents during reverse ATRP of MAN initiated by DCDPS with [MAN] = 4.5 M and [MAN]:[Initiator]:[SmCl$_3$]:[LA] = 400:1:3:2 at 70°C.

Fig. 7. Dependence of PDI on the monomer conversion in different solvents for reverse ATRP of MAN initiated by DCDPS with [MAN] = 4.5 M and [MAN]:[Initiator]:[SmCl$_3$]:[LA] = 400:1:3:2 at 70°C.

polymerization showed a decrease trend, while the molecular weight distribution of polymers remained narrow. This illustrates that a large amount of LA not only poisoned the metal catalyst, but also it had a role in catalyzing the elimination of the initiator. As more SmCl$_3$/LA catalyst system was added (entries 2, 8, 9, 10), the monomer conversion decreased and the molecular weight distributions became narrower and narrower. This illustrates that the concentration of the catalyst had a favorable influence on the activation as well as equilibrium of reverse ATRP.

3.3 Effect of Different Solvent on Reverse ATRP of MAN

To study effect of different solvents on reverse ATRP of MAN initiated by DCDPS, DMF, cyclohexanone and toluene were used as solvents, respectively. The results of these experiments are shown in Figures 5, 6, 7. The rate of polymerization was faster and the polydispersity was narrower in DMF than those in cyclohexanone and toluene.
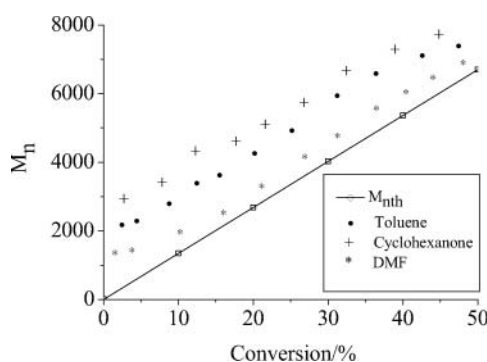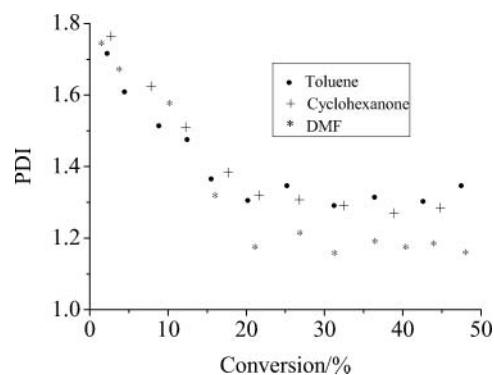
M_n of the resulting PMAN agreed better with those of the theoretical molecular weight (M_{th}) in DMF than those in cyclohexanone and toluene. The dielectric constants of the solvents are in the following order: ε_{DMF} (37.6, 20°C)> $\varepsilon_{cyclohexanone}$ (18.2, 20°C)> $\varepsilon_{toluene}$ (2.34, 20°C). When using toluene as the solvent, the polymerizations were heterogeneous due to the limited solubility of SmCl$_3$ and LA in monomer. The thermal decomposition rates of DCDPS in toluene were not high, and this might be the reason for the low amount of polymer chains, which produced higher molecular weight than that of the theoretical value (Figure 6). The addition of DMF increased the solubility of the catalyst in monomer and provided a homogeneous catalyst system. In addition, the polarity of the solvent could also affect the metal complex structure. In a polar solvent, such as DMF, Cl$^-$Sm^{2+}(lactic acid)$_2$Cl$^-$ might exist, but in a less polar solvent, (lactic acid)SmCl$_3$Sm(lactic acid) could exist. Thus, the DMF-based system provided the desired characteristics of the low polydispersity and a fast polymerization rate.

3.4 Synthesis of Block Copolymers PMAN-b-PSt

According to the mechanism polymerization of reverse ATRP, well-defined PMAN with an ω-chlorine atom end groups was obtained. Therefore, the obtained PMAN could act as a macroinitiator for the extension polymerization. For further confirmation of the controlled radical polymerization, block polymerization of styrene (St) using PMAN (M_n = 3950, PDI = 1.18) as macroinitiator was carried out at 75°C in the presence of the SmCl$_2$/LA catalyst system via a conventional ATRP process. In this study, DMF was used as the solvent. When [St] = 5.0M, [St]:[PMAN]:SmCl$_2$]:[LA] = 500:1:3:2, the block copolymer PMAN-b-PSt was with M_n = 51970, PDI = 1.35. It was clearly verified that the block copolymerization of St initiated with PMAN precursor did take place.

Fig. 6. Dependence of M_n on the monomer conversion in different solvents for reverse ATRP of MAN initiated by DCDPS with [MAN] = 4.5 M and [MAN]:[Initiator]:[SmCl$_3$]:[LA] = 400:1:3:2 at 70°C.

4 Conclusions

The new catalyst system, SmCl$_3$/LA, was successfully used in reverse ATRP of MAN in DMF with DCDPS as the initiator. Reverse ATRP of MAN initiated by DCDPS was more controlled than by AIBN. With the molar ratio of [MAN]:[DCDPS]:[SmCl3]:[LA] = 400:1:3:2, the polymerization using DMF instead of cyclohexanone and toluene as the reaction media not only showed the better control of molecular weight and its distribution but also provided the more rapid reaction rate. Negligible variation with respect to initial monomer concentration was noted. The resulting PMAN could be acted as a macroinitiator for the block polymerization of styrene.

Acknowledgments

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