

## Reversible Addition Fragmentation Chain Transfer (RAFT) Emulsion Polymerization of Methyl Methacrylate via a Plasma-initiated Process

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### Summary

The plasma-initiated emulsion polymerization of MMA in the presence of 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) was first investigated. The polymers were characterized by GPC, <sup>1</sup>H NMR, DSC and SEM. The results exhibit controlled polymerization characters: well-controlled molecular weight, relatively narrow polydispersity, molecular weight linearly increasing with conversion and successful chain extension reactions. The influence of the amount of the sodium dodecyl sulfate (SDS), CPDN concentration, plasma duration time on the polymerization rate, and micro-shape of the particle was investigated in this work. The plasma-initiation emulsion polymerization of octyl acrylate (OA) in the presence of CPDN is also carried out.

### Introduction

The advent of nitroxide-mediated polymerization (NMP) [1], atom transfer radical polymerization (ATRP) [2, 3], and reversible addition-fragmentation chain transfer (RAFT) [4] polymerization over the past decade has induced novel approaches in polymer synthesis in making complex structures with well-controlled architectures [5]. Among them, RAFT polymerization is one of the most robust “living” radical polymerization techniques. The main advantage of RAFT is that it can be used for a much wider range of functional and nonfunctional monomers and more importantly it can be used to polymerize monomers in an aqueous environment at low temperatures. The RAFT polymerization can be initiated by a traditional free radical initiator such as 2, 2'-azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) [6-10], or without a thermal or photo free radical initiator, such as the thermal RAFT polymerizations of styrene at high temperature [11, 12], the polymerizations under a constant field of <sup>60</sup>Co  $\gamma$ -radiation [13, 14] or UV radiation [15, 16] and single-pulse pulsed-laser-polymerization (SP-PLP) technique [17]. It has long been known that plasma initiation was another initiation method for the polymerization of liquid vinyl monomers [18-20]. In this technique, a radio-frequency glow discharge plasma is created in the vapor space adjacent to a condensed phase, resulting in traditional chain-growth polymerization after the plasma has been “quenched”. Plasma initiation polymerization (PIP) differs from the more familiar “plasma polymerization”, in

which active species created in the glow discharge react to deposit a highly cross-linked polymer film on a substrate placed in or near the discharge [21]. Although the mechanism involved in PIP is unsolved until now, the widely accepted mechanism involved in PIP is a free radical polymerization process [19, 22]. Recently, Zhu et al. [23] have incorporated plasma initiation technology into RAFT bulk polymerization of MMA, and well-defined poly (methyl methacrylate) (PMMA) with molecular weight distribution of low polydispersity ( $M_w/M_n$ ) could be synthesized. The maximum molecular weight ( $M_{n, GPC}$ ) reaches up to 375 000, with a relatively narrow molecular weight distribution ( $M_w/M_n = 1.17$ ) via this method. Thus, the plasma-initiation may be a promising initiation method which can be used in RAFT polymerization process. At the same time, emulsion polymerization should, in principle, make it possible to obtain higher molecular weights and faster rates of polymerization compared to homogeneous systems. Furthermore, Living radical polymerizations carried out in aqueous media [24, 25] become more important to industrial applications because of a number of advantages, such as environmental-friendly processes, easy removal of reaction heat released during polymerization, and feasible handling of the final product because of its low viscosity. The objective of this paper is to investigate the feasibility of plasma-initiated emulsion polymerization of MMA with 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) as RAFT agent and to focus on the “living”/controlled nature of the polymerization.

## Experimental

### *Materials*

The monomers, MMA and St were purchased from Shanghai Chemical Reagents Co. (Shanghai, China). They were washed with an aqueous solution of sodium hydroxide (5wt%) three times, followed by deionized water until neutralization, and then dried over anhydrous magnesium sulfate. They were distilled twice under reduced pressure and stored at -18 °C. AIBN (97%, Shanghai Chemical Reagents Co.) was recrystallized from ethanol and dried at room temperature under vacuum and stored at 4 °C. Tetrahydrofuran (THF, analytical reagent) were obtained from Yangyuan Chemical Reagents Co. (Suzhou, China). CPDN was synthesized according to the method reported in Ref 18 with the purity greater than 96% (Waters 515 HPLC;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.95 (s, 6H), 7.42 (m, 2H), 7.51 (m, 2H), 7.85 (m, 2H), and 8.10(m, 1H) ). All other chemicals (reagent or analytical grade) were obtained from Shanghai Chemical Reagents Co. and used as received.

### *Characterization*

Conversion was determined by a gravimetric analysis. The molecular weights and molecular weight distributions of the polymers were determined by a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector, using HR 1, HR 2, and HR 4 columns with molecular weight range of 100 – 500 000 calibrated with PMMA standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL·min<sup>-1</sup> operated at 30 °C.  $^1\text{H}$  NMR spectra of the polymers were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument using  $\text{CDCl}_3$  as the solvent and tetramethylsilane (TMS) as the internal standard. Scanning electron microscopy (SEM, Hitachi S-570) was used to analyze the morphology of the

synthesized PMMA particles. Differential Scanning Calorimetry (DSC, Perkin-Elmer DSC-2010) was used to determine the glass transition temperature of PMMA.

#### *Plasma-Initiated Emulsion Polymerization of MMA*

A typical operational procedure is described below. The emulsion was prepared by mixing an oil phase (containing monomer MMA, RAFT agent CPDN) with an aqueous phase (water and SDS). The mixture was then poured into a thin-walled ampoule with a magnetic agitate bar, and deaerated for three freezing-thawing cycles under vacuum. The ampoule was sealed by flame and then inserted between a pair of parallel plate electrodes connected to a radio-frequency capacitive-coupled glow discharge system, which was operated at 43.54 MHz of frequency and 100 W of power. As soon as the system was empowered to a designated level, a glow discharge was initiated in the vapor space above the frozen or partially frozen monomer in the head-space of the ampoule. (Note: when the temperature increases during the discharge, the pressure in the reactor increases accordingly, the discharge then quenches, therefore, the discharge time is usually not more than three minutes at room temperature). After a predetermined time (about several seconds) of plasma exposure, which was conducted at room temperature, the ampoule was taken out for the mixture to be thawed, and then shaken to mix plasma-induced reactive species with the mixture. The reaction mixture was agitated and kept at a prescribed temperature for post-polymerization. After a given reaction time, the ampoule was broken, the resultant latex was frozen in a refrigerator and became molten at room temperature. The precipitated phase was collected and dried in vacuo for 24 h. As a consequence, white PMMA beads were obtained.

#### *Chain-Extension Reaction and PSt-*b*-PMMA Block Copolymerization*

A mixture of MMA (or St), AIBN and above obtained PMMA, of predetermined concentration, was added into a 2 mL ampoule and bubbled with argon for 20 minutes, and then the ampoule was sealed by flame. The sealed ampoule was immersed into an oil bath (70 °C), and the rest of the procedure was the same as described above.

## **Results and Discussion**

### *Living Polymerization*

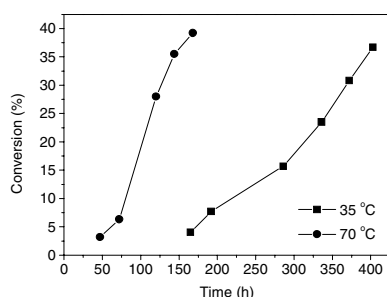
To examine the influence of reaction temperature on the polymerization performance, the polymerization reactions were conducted at 35 °C and 70 °C, respectively. The basic recipe is showed in Table 1.

Figure 1 indicates that the plots of monomer conversion versus polymerization time at 35 °C and 70 °C. The polymerization rate is slow especially at 35 °C (40 % conversion for about several weeks). There are two reasons for the slow polymerization rates. The first is that in the plasma initiation polymerization, the concentration of initiation species by the plasma discharge in the polymerization system is extremely low, and it has been reported that the plasma-initiated polymerizations proceed by a free radical mechanism and can continue for surprisingly long periods, in some cases lasting weeks, even months [18-19]. Secondly, our previous work [23] has shown that in the

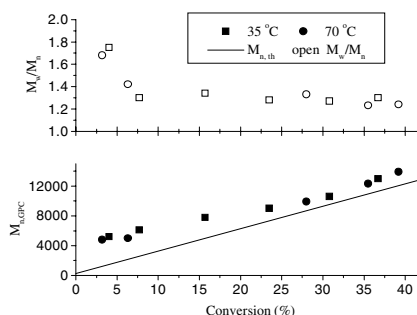
plasma-initiated polymerization of MMA in the presence of CPDN, the stationary concentration of radicals,  $[P\cdot]$ , is  $3.31 \times 10^{-10}$  L $\cdot$ mol $^{-1}$ , which is very low value compared to the concentration ( $2.11 \times 10^{-9}$  L $\cdot$ mol $^{-1}$ ) of free radicals in case of plasma-initiated polymerization of MMA without RAFT agent. Therefore, the low concentration of initiation species and low stationary concentration of radicals are together responsible for the slow polymerization rates. The higher the temperature, the higher the conversion obtained due to the fast propagation of the free radicals and possibly due to the fast addition and fragmentation reactions of RAFT agent at elevated temperature [26].

**Table 1.** Basic Recipe of Plasma-initiated Emulsion Polymerization of MMA.

Ingredients	Amount
Monomer (MMA)	1.5 mL
RAFT agent (CPDN)	0.0043-0.0128 g
Surfactant (SDS)	0.0225-0.045 g
Deionized water	5 mL
Power	100 W
Discharge duration	0 s, 30 s



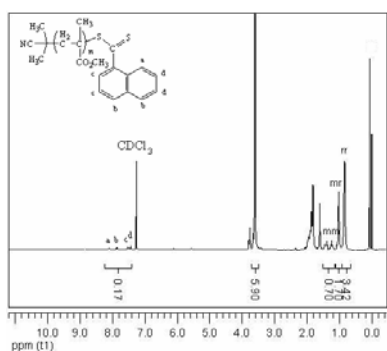
**Figure 1.** Kinetics of plasma-initiated emulsion polymerization of MMA at 35 °C and 70 °C,  $[MMA]_0 : [CPDN]_0 = 300 : 1$ . plasma: 100 W, 30 s.



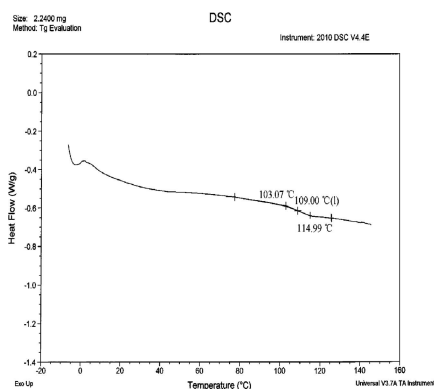
**Figure 2.** Dependence of  $M_n$  and  $M_w/M_n$  on conversion (the conditions are same as Figure 1),  $M_{n,th} = ([MMA]_0/[CPDN]_0) \times MW_{MMA} \times Conversion + MW_{CPDN}$ .

The “living”/control behavior is demonstrated in the linear evolution of the number-average molecular weight with conversion, and narrow  $M_w/M_n$ s at 35 °C and 70 °C (Figure 2). These results suggest that CPDN is an effective RAFT agent to control the plasma-initiated polymerization of MMA under the emulsion conditions. It should be mentioned here that the molecular weight ( $M_{n, GPC}$ ) is greater than the theoretical value ( $M_{n, th}$ ). The deviation from theoretical values of  $M_n$  were due to slow transformation of initial RAFT agent into polymeric RAFT agent (so-called hybrid behaviour) and the insufficient transport of RAFT agent from the droplets to the particles through the water phase [27, 28], while the theoretical value is calculated based on the complete consumption of the RAFT agent during this period.

The chain ends of PMMA prepared by the emulsion polymerization of MMA were analyzed by  $^1\text{H}$  NMR spectroscopy (Figure 3). The signals at about  $\delta = 3.61$  ppm are ascribed to the methoxyl (3H, integration =  $I_{3,6} = 5.90$ ) group of MMA, and the signals at  $\delta = 7.4$ – $8.1$  ppm are correspondent to the aromatic protons of the naphthalene (7H, integration =  $I_{7,4} = 0.17$ ) units in CPDN, indicating that the RAFT agents moieties are attached to the polymer chain ends, which confirms that the polymerization is accordant to the RAFT mechanism. Furthermore, assuming each polymer chain captured by one dithioester moiety, the molecular weight can be calculated from the integrations in  $^1\text{H}$  NMR according to the equation:  $M_{n, \text{NMR}} = (I_{3,6}/3) \times 100.12 / (I_{7,4}/7) + 272$ . The calculated  $M_{n, \text{NMR}}$  (8400) is higher than the  $M_{n, \text{GPC}}$  (5200), indicating that a portion of the polymer chain was not capped by the CPDN moiety, which could be attributed to slow diffusion of RAFT agent to the particles [29].



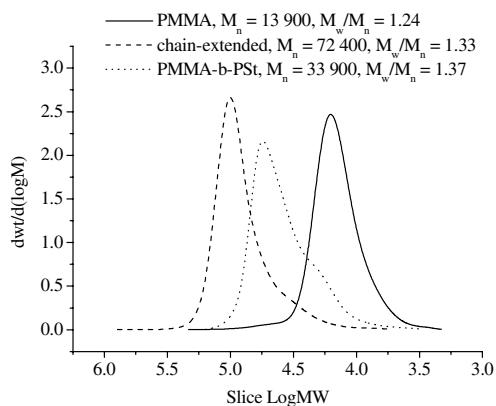
**Figure 3.**  $^1\text{H}$  NMR spectra of PMMA with  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as internal standard.  $M_{n, \text{GPC}} = 5200$ ,  $M_w/M_n = 1.75$ .



**Figure 4.** DSC thermogram of the prepared PMMA beads.

The signals at about  $\delta = 0.82$ ,  $1.02$ , and  $1.18$  ppm in Figure 3 arise from syndiotactic (rr), atactic (mr), and isotactic (mm) methyl groups, respectively [30]. The tacticity of the PMMA was calculated from the integrated ratios of rr, mr, and mm. The ratios of the triad tacticity for syndiotactic, atactic, and isotactic were 58.7, 29.2, and 12.1, respectively. The relatively regular molecular structure of the PMMA particles is expected to affect the thermal properties. In general, the glass transition ( $T_g$ ) is proportional to the degree of the syndiotacticity and inversely proportional to the degree of isotacticity. The DSC spectrum of obtained PMMA has been shown in Figure 4. From Figure 4, it can be found that the glass-transition temperature ( $T_g$ ) of the obtained PMMA is about  $109^\circ\text{C}$ , which complies with the ratio of syndiotacticity (58.7%) of the PMMA sample prepared in this study [31].

The obtained polymer (PMMA) is used as macro-RAFT agents to conduct the chain-extension with fresh MMA and styrene, respectively, using AIBN as the initiator. The GPC traces are showed in Figure 5. It can be found that the molecular weight of PMMA increases from 13900 ( $M_w/M_n = 1.24$ ) to 72400 ( $M_w/M_n = 1.34$ ) in the case of chain extension and from 13900 ( $M_w/M_n = 1.24$ ) to 33900 ( $M_w/M_n = 1.37$ ) in the case of the block copolymerization with styrene. However, the GPC trace of the chain-extended polymer shows an obvious tail, which could be caused by some dead chains in macro-RAFT agents.



**Figure 5.** GPC curves of the polymers.  $[MMA]_0 : [PMMA]_0 : [AIBN]_0 = 2000 : 2 : 1$ ,  $70\text{ }^\circ\text{C}$ , conversion = 78.7% (22 h);  $[St]_0 : [PMMA]_0 : [AIBN]_0 = 2000 : 2 : 1$ ,  $70\text{ }^\circ\text{C}$ , conversion = 23.2% (48 h).

In order to have more understandings on the emulsion polymerization of MMA by the plasma initiation, the influence of the amount of the surfactant (SDS) and CPDN concentration on the polymerization rate, and micro-shape of the particle was studied. Emulsion polymerizations were carried out according to conventional batch procedures as described in the experimental section. The results are showed in Table 2. From entry 1-3, it can be found that the polymerization rates increased with the amount of the surfactant SDS, which could be attributed to that the number of particles increased with SDS concentration during the interval I [10]. As the conversion reached to 49%, the high level of coagulum appears (see the micrograph entry 3, in Figure 6) indicating a loss of colloidal stability. In fact, a red layer appeared shortly after the commencement of polymerization in our experiments, which has also been reported by other authors [32-35]. The red layer was revealed by Brouwer to be consisted of monomer-swollen, dithiobenzoate-end-capped oligomers [35]. The diffusion of these oligomers was extremely slow on the reaction timescale, so the transportation into the particles was slow. Once the changeover from interval II to interval III had occurred during the emulsion polymerization, these dormant species coalesced together to form the red coagulant [32]. The SEM micrographs of PMMA beads (entry 1-3) shown in Figure 6 indicates that they had a similar particle size distribution and micro-shape of the particle, the possible reason may be the change of amount of SDS was slight, or not in a wider range [10]. From the entry 1, 4 and 5, it can be found that the polymerization rate decreased with the concentration of CPDN, i. e. the retardation phenomenon [36-39] happened. There are several opinions to explain the retardation. Barner-Kowollik and coworkers [36] concluded that retardation was due to slow fragmentation of the intermediate radicals. They also suggested that the reversible macroRAFT radical termination or stable macroradical sink (radical or nonradical storage) [37] was likely to be responsible for the rate retardation. Monteiro et al. [38] and Kwak et al. [39] considered that it was caused by the cross-termination, i.e. the termination between the propagation free radical  $P\cdot$  and intermediate  $P-(X\cdot)-P$ . Comparing the entry 1 with 6, it is not difficult to find that the conversion was highly elevated by the introduction of plasma initiation, indicating the initiating radicals are generated mainly from the plasma initiation.

**Table 2.** Effects of reaction conditions on the emulsion polymerization of MMA.

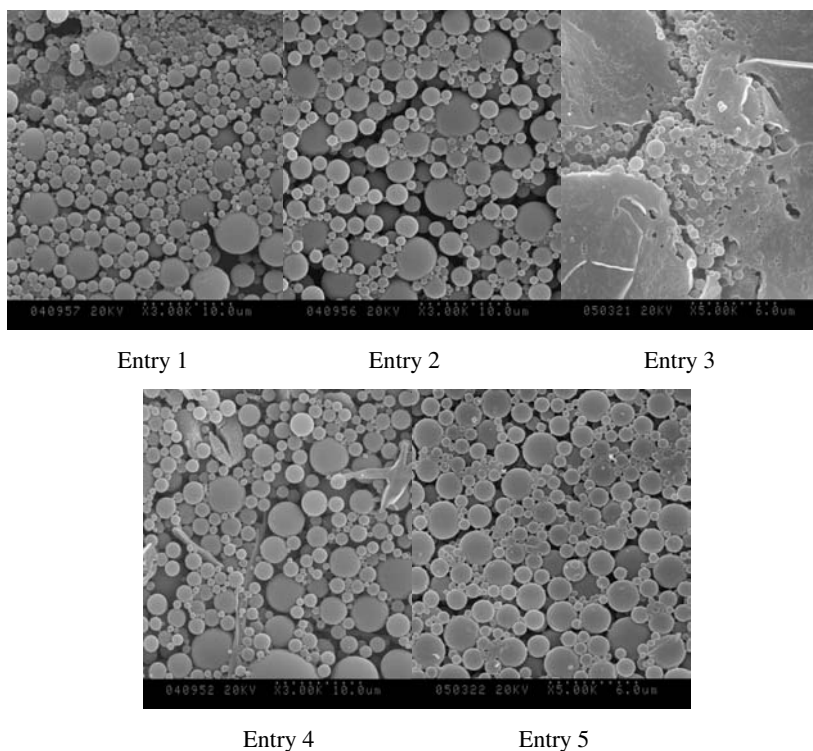
Entry (a)	[MMA] <sub>0</sub> : [CPDN] <sub>0</sub>	SDS (g) <sup>(b)</sup>	Conversion (%)	M <sub>n, GPC</sub>	M <sub>w</sub> /M <sub>n</sub>	M <sub>n, th</sub> <sup>(c)</sup>
1	300 : 1	0.0225	11.0	5700	1.67	3600
2	300 : 1	0.03	26.0	10300	1.36	8100
3	300 : 1	0.045	49.0	21900	1.23	15000
4	600 : 1	0.0225	17.0	12400	1.49	10500
5	900 : 1	0.0225	23.0	21000	1.33	21000
6 <sup>(d)</sup>	300 : 1	0.0225	2.0	6300	2.49	900

(a). polymerization is conducted at 70 °C, 96 h; power: 100 w, discharge duration: 30 s

(b). in 5 mL H<sub>2</sub>O

(c).  $M_{n, th} = ([MMA]_0/[CPDN]_0) \times MW_{MMA} \times Conversion + MW_{CPDN}$

(d). no discharge

**Figure 6.** SEM micrographs of PMMA beads.

#### *Plasma-initiated Emulsion Polymerization of OA*

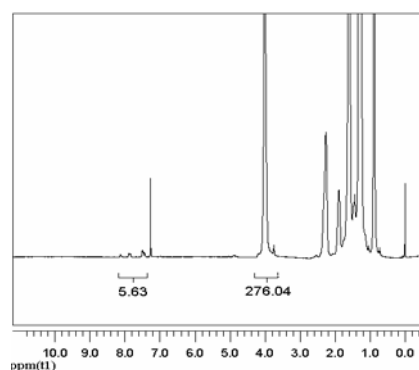
To test the generality of the emulsion polymerization of other monomers by plasma initiation in the presence of RAFT agent, octyl acrylate (OA) was then polymerized mediated by CPDN under the same reaction conditions (Table 3). Well-defined polymers with narrow  $M_w/M_n$ s were also obtained.

**Table 3.** Emulsion polymerization of OA by plasma initiation.

Entry <sup>(a)</sup>	Time (h)	Conversion (%)	$M_{n, GPC}$	$M_w/M_n$	$M_{n, th}$ <sup>(b)</sup>
7	48	trace	-	-	-
8	136	3.0	7300	1.53	3100
9	236	13.6	12600	1.39	12800
10	356	18.9	17800	1.30	17700
11	480	28.0	27800	1.32	26100

(a). polymerization is conducted at 70 °C;  $[OA]_0 : [CPDN]_0 = 500 : 1$ ; 0.03 g SDS in 10 mL H<sub>2</sub>O, Oil: water = 1.5 : 5 (v/v); plasma : 100 w, 30 s

(b).  $M_{n, th} = ([OA]_0/[CPDN]_0) \times MW_{OA} \times Conversion + MW_{CPDN}$



**Figure 7.** <sup>1</sup>H NMR spectra of POA with CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard.  $M_{n, GPC} = 27\ 800$ ,  $M_w/M_n = 1.32$ ,  $M_{n, NMR} = 31\ 600$ .

The polymer was also measured by <sup>1</sup>H NMR, shown in Figure 7. The signals at about  $\delta = 4.08$  ppm are ascribed to the methylene (2H, intergration =  $I_{4.08} = 276.04$ ) attached at the ester group of OA. The CPDN moieties can also be found from the signals at 7.1-8.4 ppm (7H, intergration =  $I_{7.4} = 5.63$ ). The  $M_{n, NMR}$  can be calculated from the integrations in <sup>1</sup>H NMR according to the equation:  $M_{n, NMR} = (I_{4.08}/2) \times 184.27 / (I_{7.4}/7) + 272$ . (31 600), which is a little higher than the  $M_{n, GPC}$  (27 800), the reason has been explained previously. All the above demonstrated that the polymerization of OA was also well controlled in emulsion.

## Conclusions

Well-defined PMMA by plasma-initiated emulsion polymerization in the presence of CPDN was achieved. The polymerization demonstrated “living”/controlled features with the predictable number-average molecular weights and narrow molecular weight distributions of the resultant polymers capped by the CPDN moieties. However, a loss of colloidal stability could be found as the conversion reached to 49%, which was the same as the phenomena in the conventional RAFT/ emulsion polymerizations. Further researches indicated that the plasma-initiated emulsion polymerization in the CPDN can also be applied to octyl acrylate (OA), and the polymerization also well-controlled.



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