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Study on controlled free-radical polymerization in the presence of 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN)

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Abstract

Polymerization of methyl methacrylate was carried out in the presence of 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN). The results exhibit controlled polymerization characters: well-controlled molecular weight, narrow polydispersity (minimal value: 1.09), molecular weight linearly increasing with conversion and first-order kinetics of polymerization. The polymer can be used to synthesize methyl methacrylate–styrene copolymer with narrow polydispersity (minimal value: 1.22). The polymers were characterized by ^{1}H NMR and GPC. The effect of molar ratio among MMA/CNDB/AIBN on polymerization was investigated. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Controlled polymerization; Reversible addition fragmentation transfer reactions; 2-cyanoprop-2-yl 1-dithio naphthalate (CPDN)

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1. Introduction

In recent years, considerable attention has been paid to living/controlled free radical polymerization [1,2]. Ideally, these polymerizations can synthesize polymers with predetermined molecular weight; narrow polydispersity and these polymers even can be reactivated for chain extension or block polymer synthesis under relatively simple conditions. Several methods for achieving controlled/living radical polymerization have been developed; such as atom transfer radical polymerization (ATRP) [3], and nitroxyl radical mediated polymerization (NMP) [4]. However these polymerization methods have limitations, such as the polymerization shows controlled characters on a narrow range of monomers; expensive agent used and the obtained polymers contain metal ions, etc. The CSIRO group has recently developed a novel living radical polymerization so called reversible addition fragmentation transfer polymerization (RAFT) [5]. Compared with other living free radical polymerization methods, RAFT polymerization has some advantages: (a) it can be applied to a wide range of monomers including functional monomers containing acid [6], hydroxy, amino groups [7]; (b) obtained polymers with well-controlled molecular weight and narrow polydipersity; (c) the polymerization condition is the same as conventional radical polymerization; and (d) the polymers do not contain metal ions.

The RAFT polymerization has already been used in many polymerization situations, such as bulk polymerization, solution polymerization [8], emulsion polymerization [9] etc. Many special structure polymers, such as block copolymers [10], star copolymers [11], even graft polymers on the solid surface [12], have been synthesized through RAFT polymerization. It differs from ATRP and NMP, in which molecular weight control is established via fast, reversible chain termination, RAFT polymerization control the molecular weight via fast, reversible chain transfer to a thio-compound, such as dithioester [13], trithiocarbonate [14], or dithiocarbamate [15]. The mechanism is showed in Scheme 1 [16].

Different Z and R groups would affect the activity of RAFT agents [17]. Usually, R should be a good free radical leaving-group both in absolute terms and relative to the propagating species derived from the monomer being polymerized. While the reactivity of the C=S double bond would be affected by Z group. CSIRO group has reported that the reactivity of RAFT agents with different Z group decreases in this way: aryl > alkyl ≈ alkylthio ≈ pyrrole > aryloxy > amido > alkoxy > dialkylamino. In most cases, phenyl is used as Z group while cumyl or isobutylcyanate is used as R group.

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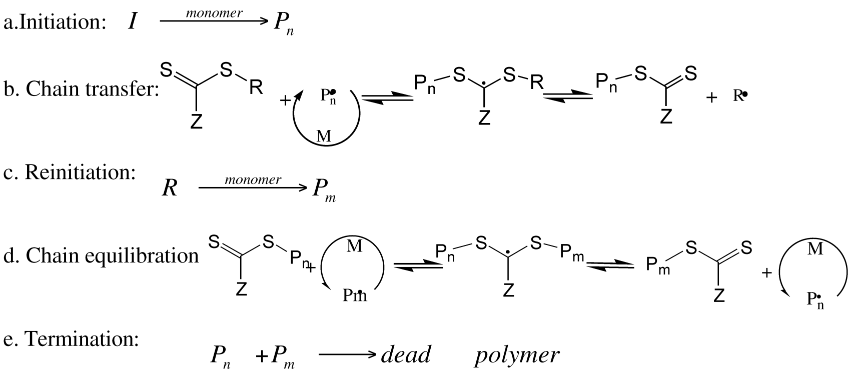


Scheme 1. Mechanism of reversible addition–fragmentation chain transfer (RAFT) reaction.

In this article, we have synthesized a dithioester CPDN and used as RAFT agent to conduct the polymerization of methyl methacrylate (MMA) in benzene solution.

2. Experimental

2.1. Materials

1-Bromonaphane and carbon disulfide were dried over 4 Å molecular sieve at least 2 weeks before use. AIBN was recrystallized from ethanol and dried at room temperature under vacuum and stored in the refrigerator at −15 °C. MMA and styrene (St) were washed with NaOH solution, dried over anhydrous $MgSO_4$ and then distilled under reduced pressure prior to use. All the other materials were treated with standard methods prior to use.

2.2. Synthesis of CPDN

CPDN was prepared according to the method described in Ref. [5] (see Scheme 2). A solution of 22.5 g (0.11 mol) 1-bromonaphane and 90 ml THF was added to a 250 ml bottle containing magnesium (2.88 g, 0.118 mol) within 1 h and refluxed for 1 h. Carbon disulfide 8.36 g (0.11 mol) was added to the solution at room temperature and refluxed for 8 h. The mixture was poured into water and acidified by diluted hydrochloric acid. The solution was extracted with chloroform (40 ml × 3). After evaporated under vacuum, the resident added with 18 ml ethyl acetate and reacted with 4.7 g DMSO under nitrogen protection for 10 h. The mixture was added with 12.24 g AIBN and refluxed for another 15 h. After evaporation of the solvent, crude CPDN was obtained. The pure CPDN was obtained as a solid by chromatography on silica gel column with petroleum ester–ethyl acetate = 10:1 as eluant as a dark red oil (12.89 g, 40.2%), when kept in the refrigerator at −18 °C. HPLC (waters 515) indicated that the purity is above 96%, attempt to purify further failed, the impurity may be slightly decomposition of the product in the process of purify. ^1H NMR ($CDCl_3$), 1.95 (s, 6H); 7.42 (m, 2H); 7.51 (m, 2H); 7.85 (m, 2H) and 8.10 (m, 1H).

2.3. RAFT polymerization of MMA

A mixture of predetermined concentration of MMA, benzene, AIBN and CPDN was added to a 2 ml amps. The system was sealed after bubbled with nitrogen for 20 min to eliminate oxygen. After reacting at predetermined time and temperature, the seal was opened and the mixture was diluted with a little THF and then precipitated in methanol. The polymer was filtered and dried at 40 °C under vacuum for 48 h. The conversion was determined by gravimetrically.

2.4. St-MMA copolymerization use PMMA as macro-RAFT agent

The same procedure as RAFT polymerization of MMA was used except CPDN was substituted by PMMA obtained from MMA RAFT polymerization.

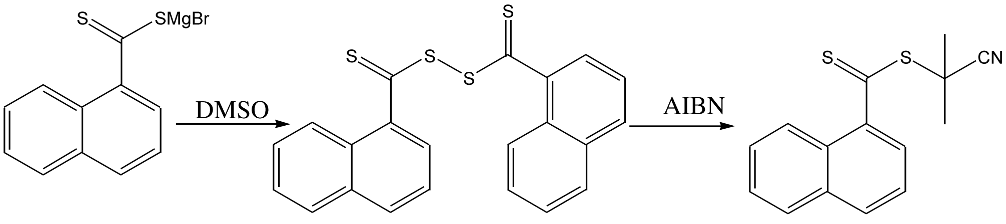
2.5. Characterization

The molecular weight (M_n) and polydispersity (PD) were measured on a Waters 1515 gel permeation chromatograph (GPC) using tetrahydrofuran as the eluent at a flow rate of 1.0 ml min^{-1}. Molecular weights were determined from standard polystyrene calibration. ^1H NMR spectra of the polymers were recorded on a NAVA400 nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard.

3. Results and discussion

3.1. Living radical polymerization of MMA use CPDN as RAFT agent

There are some experimental criteria to determine a controlled/'living' polymerization [18]. Among these criteria, some are crucial: narrow polydispersity, controlled molecular weight, linear relationship between molecular weight and monomer conversion and constant concentration of active centers during the polymerization. In this article,



CPDN

Scheme 2. Preparation route of 2-cynoprop-2-yl 1-dithionaphthalate (CPDN).

CPDN used as RAFT agent to conduct MMA polymerization. The RAFT agent CPDN was prepared via a combined reaction of bromomagnesium 1-dithionaphthalate along with a radical reaction with AIBN (Scheme 2).

The compound was examined as chain-transfer agent in the RAFT polymerization of MMA. Fig. 1 is the ^{1}H NMR spectrum of polymer ($M_n = 9253$, PDI = 1.12) obtained by polymerization of MMA using CPDN and AIBN as initiating system. The signals at $\delta = 7.4$–8.1 ppm correspond to the aromatic protons of CPDN units. The appearance of the signals at $\delta = 7.4$–8.1 ppm indicates that the dithioester formed from CPDN reacted with primary or propagating radicals (Scheme 1, b and d), and that the CPDN moiety remained at the end of polymer chain.

A linear relationship between $\ln([M]_0/[M])$ and reaction time is shown in Fig. 2. The first-order kinetics indicates that the concentration of free radicals remained constant during the polymerization. The plots of M_n and polydispersity versus monomer conversion of MMA are shown in Fig. 3. M_n values increased linearly with conversion, while the polydispersity remained in a relative low value (1.1–1.2). These results are similar as results reported by CSIRO group [8,13,14] suggested that CPDN perform effective RAFT agent to control the polymerization of MMA at the experiment conditions.

Furthermore, the polymers (PMMA) obtained from the RAFT polymerization have been used as a macro-RAFT agent to conduct polymerization of styrene using AIBN as initiator. The GPC spectrum of these block polymers is shown in Fig. 4. There is an obvious peak shift from the macro-RAFT to the MMA–PS block copolymer in the result. The peak of PMMA macro-RAFT agent is disappeared thoroughly, which demonstrated that the macro-RAFT agent has converted to a PMMA-*b*-PS copolymer. The curve of GPC spectrum shows a single peak and the peak shape agrees well with Gauss distribution. No shoulder peak has been found in the GPC spectrum. The molecular weight increased when the polymerization time is being prolonged. On the other hand, the PMMA-*b*-PS polydispersity is a little larger than that of PMMA macro-RAFT agent (from 1.133 to 1.300 and 1.223). This may cause by the little portion homopolyerization of styrene initiated by AIBN and the dead polymer (about 3%) existed in macro-RAFT agent [22,23].

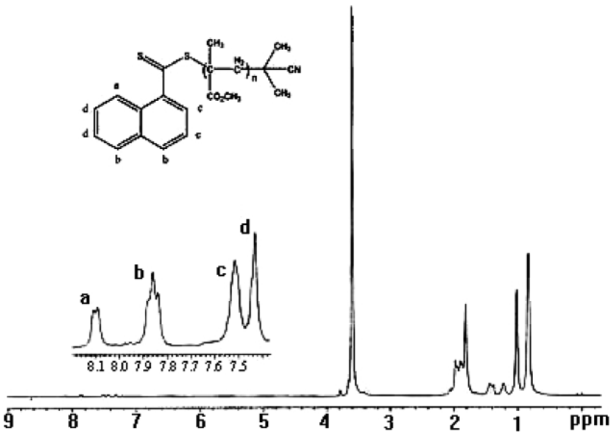


Fig. 1. ^{1}H NMR of PMMA ($M_n = 9253$, PDI = 1.12) polymer use $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard.

3.2. Influence of different CPDN and AIBN ratio

Based on the RAFT polymerization mechanism (shown in Scheme 1), the ratio of CPDN and AIBN should have a significant influence on the polydispersity of polymer. Increasing the concentration of initiator and lowering the amount of RAFT agent will slow down the transformation

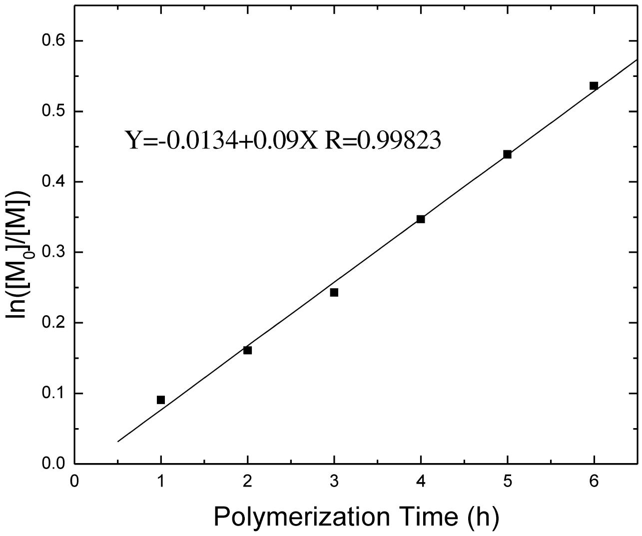


Fig. 2. Relationship between $\ln([M]_0/[M])$ and polymerization time for RAFT polymerization of MMA at 60 °C, $[MMA]_0/[CPDN]_0/[AIBN]_0 = 500:1:0.5$.

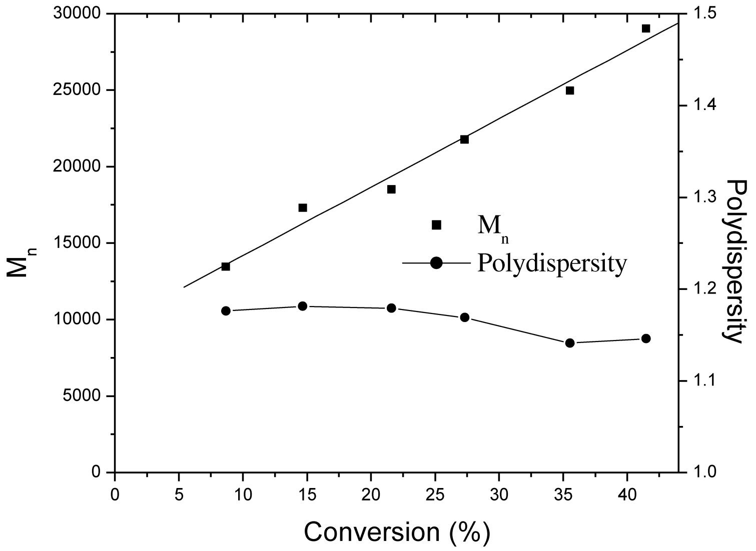


Fig. 3. Dependence of molecular weight M_n and polydispersity on monomer conversion for the RAFT polymerization of MMA at 60 °C, $[MMA]_0/[CPDN]_0/[AIBN]_0 = 500:1:0.5$.

of CPDN into dormant polymer chains. At the same time, the probability of termination between two radicals increases. As a result, the obtained polymer has a broader polydispersity. The influence of different CPDN and AIBN ratio on the molecular weight and polydispersity has been carried out. The results are listed in Table 1 and Fig. 5. The theoretical number average molecular weight ($M_{n,Cal.}$) could be calculated according to following equation:

$$M_{n,Cal.} = \frac{\text{monomer weight}}{\text{mole of CPDN}} \times \text{conversion}$$

The results in Table 1 show that the discrepancy between $M_{n,Cal.}$ and molecular weight estimated by GPC ($M_{n,GPC}$) increases as the ratio of CNDB/AIBN decrease. The

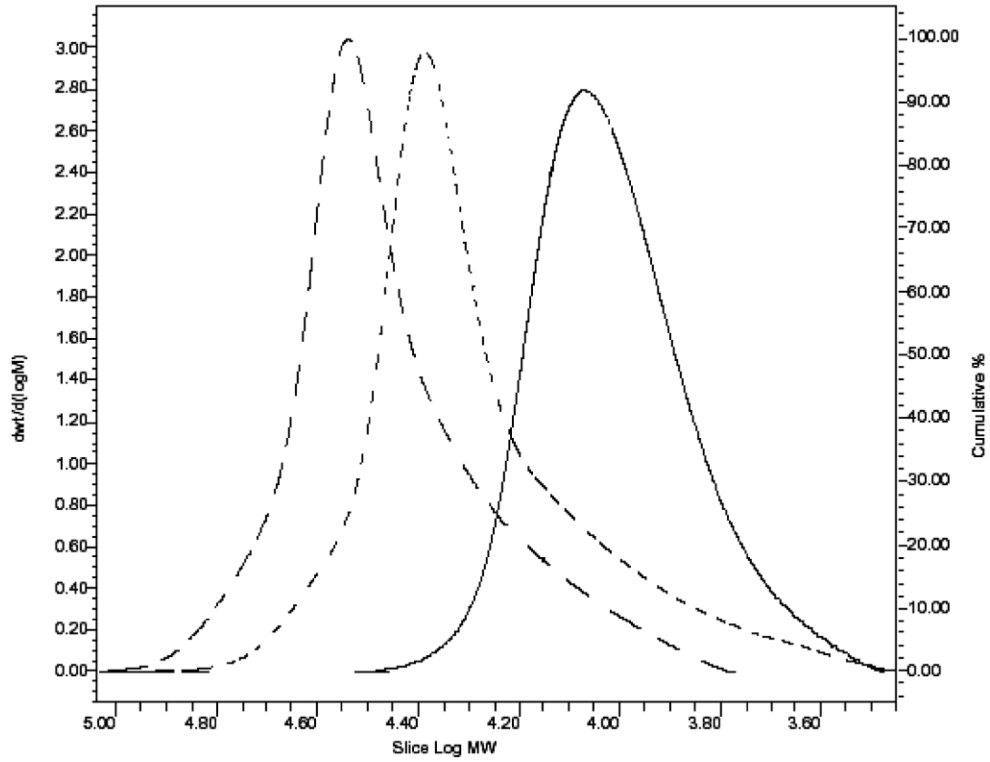


Fig. 4. GPC results of PMMA monopolymer and PMMA–PS copolymers with different reaction time. — PMMA RAFT polymer, $M_n = 9712$, polydispersity = 1.133; - - - PMMA-*b*-PS copolymer with 480 min, $M_n = 16704$, polydispersity = 1.300; – – – PMMA-*b*-PS copolymer with 660 min, $M_n = 25{,}742$, polydispersity = 1.223.

Table 1
Molar mass and conversion data for PMMA samples prepared via different CPDN and AIBN mole ratio at 60 °C

Sample	MMA (mmol)	Benzene (ml)	AIBN (mmol) $\times 10^2$	CNDB (mmol) $\times 10^2$	Time (h)	$M_n \times 10^{-3}$ (GPC)	$M_n \times 10^{-3}$ (Cal.)	PD	Conv (%)	CNDB/AIBN (mole ratio)
PMMA11	9.44	1	3.05	12.20	20	16958	5807	1.12	74.93	4:1
PMMA12	9.44	1	3.05	9.15	20	16958	9336	1.16	90.35	3:1
PMMA13	9.44	1	3.05	7.60	20	22037	11051	1.16	88.83	2.5:1
PMMA14	9.44	1	3.05	6.10	20	23359	15082	1.23	97.30	2:1
PMMA15	9.44	1	3.05	5.49	20	27029	17222	1.25	99.98	1.8:1
PMMA16	9.44	1	3.05	4.58	20	28763	20161	1.32	97.66	1.5:1
PMMA17	9.44	1	3.05	3.05	20	33624	28827	1.47	92.99	1:1
PMMA18	9.44	1	3.05	2.44	20	39666	38750	1.50	100	0.8:1
PMMA19	9.44	1	3.05	1.53	20	41225	61798	1.56	100	0.5:1

discrepancy reaches a maximum value when the ratio is 0.8:1.

The results in Table 1 also indicate that the molecular weight was not determined by the mole ratio of [monomer]/[AIBN], but by the ratio of [monomer]/[CPDN]. At lower molar ratio of [CPDN]/[AIBN] (0.8:1 and 0.5:1), broader values of polydispersity (1.5 and 1.56) were observed. This result was caused by some of the primary radicals took part in the initiation propagation and irreversible termination of some radicals at low ratio of [CPDN]/[AIBN]. At high molar ratio of [CPDN]/[AIBN], narrower polydispersity was obtained, which is consistent with the prediction based on the proposed mechanism in Scheme 1. The polydispersity of polymer decreased to a very low value and did not change very much as the mole ratio of [CPDN]/[AIBN] is higher than 2.5:1.

The results in Fig. 5 show that the polymerization rate decreases as the ratio of $[\mathrm{CPDN}]_0/[\mathrm{AIBN}]_0$ increases, which results from the decrease in free radical concentration as $[\mathrm{AIBN}]_0$ decreases. There is an obvious retardation phenomenon in the polymerization. The retardation in rate is enhanced as the ratio of $[\mathrm{CPDN}]_0/[\mathrm{AIBN}]_0$ increases from 1:1 to 1:0.5. There are two opinions to explain the retardation. Davis et al. [17,19] assumed that the retardation may cause by specificity for the expelled radical (R•) to add to the RAFT agent rather than to monomer as the ratio of $[\mathrm{CPDN}]_0/[\mathrm{AIBN}]_0$ increased. Monteiro et al. [20] and Kwak et al. [21] considered that it was caused by the cross-termination, i.e. the termination between the propagation free radical P• and intermediate P–(X•)–P.

3.3. Influence of different mole ratio of different MMA and CPDN

According to the mechanism shown in Scheme 1, in order to control the polymerization process, the concentration of RAFT agent must be higher than a value. Therefore, a study of the polymerization of MMA at various molar ratios of $[\mathrm{MMA}]_0/[\mathrm{CPDN}]_0$ was carried out at 60 °C. The results are shown in Table 2. The polydispersity increased as the mole ratio of $[\mathrm{MMA}]_0/[\mathrm{AIBN}]_0$ increased.

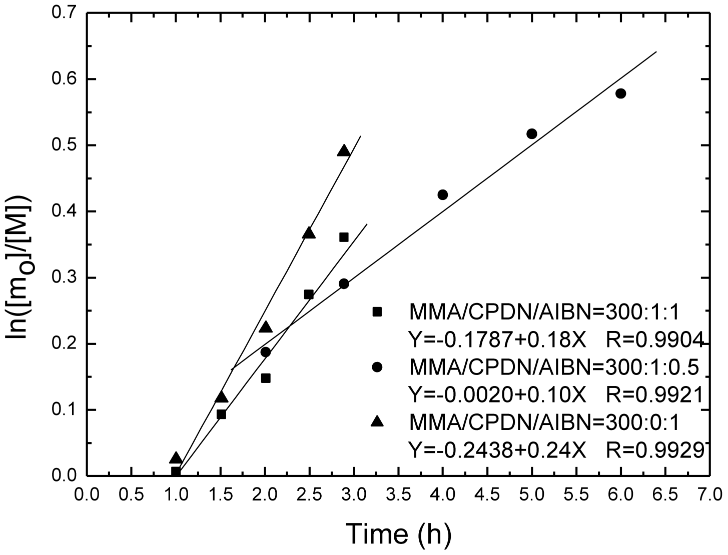


Fig. 5. Relationship between $\ln([\mathrm{M}_0]/[\mathrm{M}])$ and polymerization time under different mole ratio of $[\mathrm{MMA}]_0/[\mathrm{CPDN}]_0/[\mathrm{AIBN}]_0$ with the reaction temperature of 60 °C.

Table 2
Molar mass and conversion data for polymathyl methacrylate samples prepared via different MMA and CPDN mole ratio at 60 °C

Sample	MMA (mmol)	Benzene (ml)	AIBN (mmol) × 10^2	CNDB (mmol) × 10^2	Time (h)	$M_n \times 10^{-3}$ (GPC)	$M_n \times 10^{-3}$ (Cal.)	PD	Conv (%)	$[MMA]_0/[CNDB]_0$
PMMA21	9.44	1	2.360	4.72	20	29113	18968	1.25	94.69	200:1
PMMA22	9.44	1	1.575	3.15	20	33979	27506	1.42	91.54	300:1
PMMA23	9.44	1	0.945	1.89	20	45692	50080	1.56	100	500:1
PMMA24	9.44	1	0.590	1.18	20	65380	63766	1.60	79.58	800:1
PMMA25	9.44	1	0.472	0.944	20	43800	53776	1.69	53.69	1000:1
PMMA26	9.44	1	0.315	0.625	20	81487	83954	2.09	55.88	1500:1

The polydispersity remains in the relative low value, when the mole ratio of $[MMA]_0/[AIBN]_0$ is lower than 1000:1.

4. Conclusion

The RAFT polymerization of MMA using CPDN as RAFT agent and AIBN as initiator shows controlled free radical characters: linear relationship between molecular weight and monomer conversion and first-order kinetics of the polymerization. The obtained polymers have been successfully used as a macro-RAFT agent to conduct the polymerization of styrene.

Acknowledgements

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