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Study on MMA and BA Emulsion Copolymerization Using 2,4-Diphenyl-4-methyl-1-pentene as the Irreversible Addition–Fragmentation Chain Transfer Agent

Zuxin Zhang , Daihui Zhang , Gaowei Fu, Chunpeng Wang, Fuxiang Chu and Riqing Chen *

Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry; National Engineering Laboratory for Biomass Chemical Utilization; Key Laboratory of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; Key Laboratory of Biomass Energy and Material, Nanjing 210042, China; zinc2019@163.com (Z.Z.); zdh0824@163.com (D.Z.); 15638863071@163.com (G.F.); wangcpg@163.com (C.W.); chufuxiang@caf.ac.cn (F.C.)

* Correspondence: michaelmao77@163.com; Tel.: +86-025-8548-2519

Received: 14 December 2019; Accepted: 1 January 2020; Published: 2 January 2020



Abstract: As a chain transfer agent, 2,4-diphenyl-4-methyl-1-pentene (α MSD) was first introduced in the emulsion binary copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA) based on an irreversible addition–fragmentation chain transfer (AFCT) mechanism. The effects of α MSD on molecular weight and its distribution, the degree of polymerization, polymerization rate, monomer conversion, particle size, and tensile properties of the formed latexes were systematically investigated. Its potential chain transfer mechanism was also explored according to the ^1H NMR analysis. The results showed that the increase in the content of α MSD could lead to a decline in molecular weight, its distribution, and the degree of polymerization. The mass percentage of MMA in the synthesized polymers was also improved as the amounts of α MSD increased. The chain transfer coefficients of α MSD for MMA and BA were 0.62 and 0.47, respectively. The regulation mechanism of α MSD in the emulsion polymerization of acrylates was found to be consistent with Yasumasa's theory. Additionally, monomer conversion decreased greatly to 47.3% when the concentration of α MSD was higher than 1 wt% due to the extremely low polymerization rate. Moreover, the polymerization rate was also decreased probably due to the desorption and lower reactivity of the regenerative radicals from α MSD. Finally, the tensile properties of the resulting polyacrylate films were significantly affected due to the presence of α MSD.

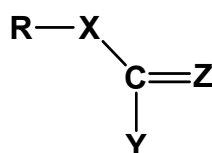
Keywords: 2,4-diphenyl-4-methyl-1-pentene; irreversible addition–fragmentation chain transfer; emulsion polymerization; MMA; BA

1. Introduction

Due to the growing environmental concerns, emulsion polymerization has become a vital method for polymer production with its environmentally friendly process, high polymerization rate, high monomer conversion, and excellent heat dissipation performance [1]. Many engineering efforts have also been put on the multiscale modeling of this process [2,3]. Chain transfer agent (CTA) as an important component, including reversible addition–fragmentation chain transfer (RAFT) and traditional CTAs, have been widely employed to control the molecular weights of synthesized polymers during the emulsion polymerization. Although many works about RAFT CTAs have recently been conducted, the complex processes and strict operation conditions of RAFT CTAs limit their wide applications. [4–6] For traditional CTAs, including mercaptans [7–10], alcohols [11], and halides [12],

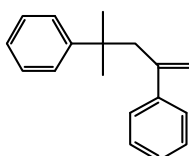
several disadvantages have also been observed, such as an unpleasant smell for mercaptans and serious environmental pollution for halides. In the case of alcohols, the amount used as a molecular weight regulator in the polymerization is typically large (10%–20% relative to monomer mass), and it is also not considered to be an environmentally friendly agent.

An irreversible addition–fragmentation chain transfer (AFCT) agent has been developed to solve the above problems. It displayed higher chain transfer efficiency, lower toxicity, and lower dosage. The first report about the AFCT agent was presented in 1988, when Meijs et al. [13] used α -benzyl-oxy-styrene as a chain transfer agent for the preparation of poly(methyl methacrylate) and polystyrene with low molecular weights. Then, various new types of AFCT agents were reported in research papers [14–21] and patents [22–24]. The common structure of the irreversible AFCT agent is shown in Scheme 1. C=Z is a double bond that is vulnerable to be attacked by the chain radical. R-X is a single bond that can be broken easily, and Y is a group to activate the reaction. The general mechanism for the irreversible AFCT agent mainly contains three steps. Firstly, the chain radical is added to the unsaturated double bond of C=Z. Then, the addition product offers a leaving group radical (R•) by the decomposition. Eventually, the novel radical reinitiates the polymerization process.



Scheme 1. General chemical structure of the irreversible addition–fragmentation chain transfer (AFCT) agent.

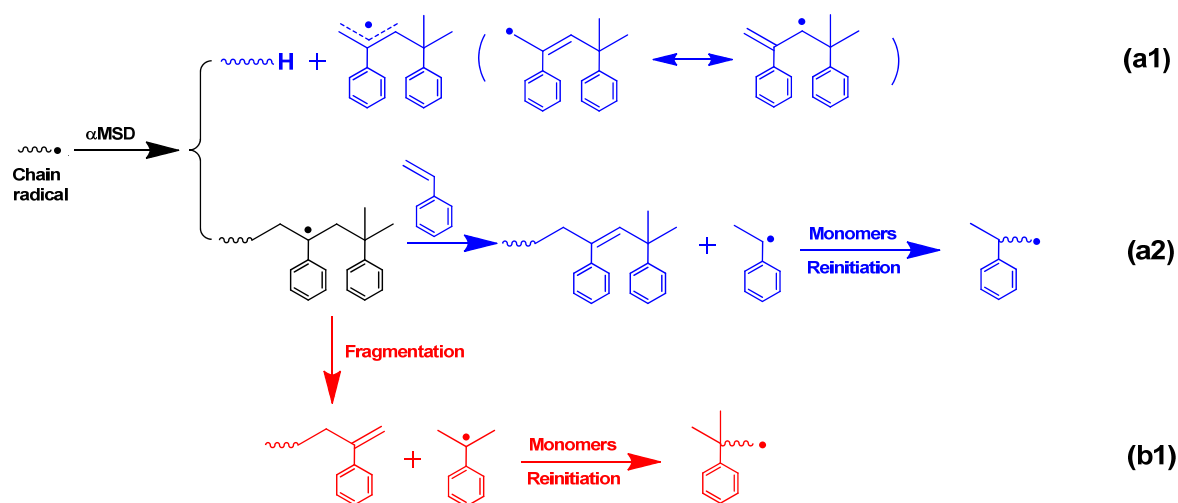
2,4-Diphenyl-4-methyl-1-pentene (α MSD), shown in Scheme 2, is a typical irreversible AFCT which can be prepared by α -methylstyrene dimerization in the presence of an aqueous sulfuric acid catalyst in the liquid–liquid mode of operation [25,26].



Scheme 2. Chemical structure of 2,4-diphenyl-4-methyl-1-pentene (α MSD).

Currently, α MSD has been introduced into solution and bulk radical polymerization in order to synthesize polystyrene with decreased molecular weights and narrowed molecular weight distribution [27,28]. For the specific regulation mechanism of α MSD in the polymerization (Scheme 3) Fisher et al. [29] proposed that the chain transfer would proceed in two cases. In the first case, alkyl hydrogen carrying a free electron abstracted from an α MSD was combined with a chain radical to form a dead chain (Scheme 3a1), whereas the residual structure of α MSD carrying a free electron could reinitiate the polymerization process (Scheme 3a1). In the second case, a chain radical was directly added to α MSD and then formed a transient state radical. An alkyl hydrogen radical divided from the α MSD structure of the latter radical was then transferred to a monomer to form a new radical. Afterwards, the new radical was able to reinitiate the polymerization. Finally, the residual part of the transient state radical became a dead chain, and the end group of the dead chain was an internal olefin (Scheme 3a2). However, according to the results of the thermal polymerization of styrene, Yasumasa et al. [30] concluded that the polymer chain radical would first be added to the terminal double bond of α MSD to produce an intermediate radical, and then this radical would decompose into a polymer chain with a terminal double bond and a cumyl radical. Finally, the cumyl radical would reinitiate the polymerization (Scheme 3b1) [31–34]. Furthermore, the regulation mechanism study of

α MSD in the radical bulk and suspension polymerization of styrene has been observed to support Yasummasa's theory.



Scheme 3. The two chain transfer mechanisms of α MSD in the polymerization of styrene. Mechanism of alkyl hydrogen suggested by Fisher et al.: transferring to chain radical (a1) and monomers (a2). (b1) Addition–fragmentation chain transfer mechanism reported by Yasummasa et al.

Although there have been some developments for the radical bulk and suspension polymerization using α MSD, its utilization in the emulsion polymerization has never been reported. In the present study, different levels of α MSD were incorporated into poly-(meth) acrylate emulsion via the semi-continuous emulsion copolymerization of MMA and BA to investigate its effects on the properties of the resulting polymer emulsion, such as molecular mass, polymerization rate, and particle size. The α MSD regulation mechanism was also discussed.

2. Materials and Methods

Reagents: α MSD (Shanghai Dibo Chemical Technology, Shanghai, China), MMA and BA (monomers), nonylphenol polyoxyethylene ether (NP-10, nonionic emulsifier), alkyl phenol ether sulfosuccinate sodium salt (OS, nonionic emulsifier), sodium dodecyl sulfate (SDS, anionic emulsifier), disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, stabilizer, Sinopharm Chemical Reagent, Shanghai, China), and ammonium persulfate (APS, initiator, Nanjing Reagent, Nanjing, China) were used as received. Distilled deionized water (DDW) was used as the reaction medium.

Emulsion polymerization: The emulsion polymerization of (meth) acrylates was carried out in a 500 mL 4-neck glass reactor equipped with a mechanical stirrer, a reflux condenser, a nitrogen gas inlet, and a thermometer. These following substances and amounts were mixed into the DDW (158.40 g): SDS (2.60 g), NP-10 (0.65 g), OS (0.65 g), and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (0.40 g), followed by mechanical stirring to form an aqueous solution. The (meth) acrylate monomers MMA (65 g) and BA (65 g) were homogeneously mixed with various amounts of α MSD under a mechanical stirring. The formed organic phase was then added dropwise into the aqueous solution to form an emulsion solution. A total of 10 g of the resulting solution and 0.55 g of initiator solution (0.05 g APS in 0.50 g DDW) were poured into the glass reactor and then heated to 75 °C. Finally, a residual pre-emulsion and 6.6 g of initiator solution containing 0.60 g APS were added dropwise simultaneously into the reactor to polymerize at 75 °C for 4 h under a nitrogen atmosphere.

Characterization: Monomer conversion was determined by a gravimetric analysis of samples withdrawn from the glass reactor during polymerization, and these samples were quenched and dried at 120 °C for 2 h. The conversion calculations were based on the total amount of solid of each emulsion sample taken at the beginning of the polymerization. The number and weight-average molecular

weights of the polymers were obtained by the gel permeation chromatography (GPC) via a Malvern Viscotek3580 system, which was calibrated using standard narrow molecular weight polystyrene samples. The dried polymer films were dissolved in GR-grade tetrahydrofuran eluent and filtered through a polytetrafluoroethylene (PTFE) filter (0.22 μm) before the injection. Analysis was conducted with a flow rate of 1 mL per minute at 40 °C. Average particle size (d_p , light intensity-weighted) and particle-size distribution index (PDI) were measured by a laser light-scattering method using a Malvern ZETASIZER Nano at 25 °C. All latex samples for the measurement were diluted 50 times with DDW. The PDI was a dimensionless coefficient denoting the broadness of the distribution diameter, and it was produced by a second-order method of cumulant analysis [35].

The ^1H NMR spectra of the resultant polymers were measured with a Bruker DMX 300 NMR. The polymer samples were dissolved into CDCl_3 (10–15 wt/vol %) at 25 °C. The tensile properties of the dried polymer films were measured on electronic tensile machine CMT7504 with a crosshead speed of 50 mm/min and a load cell of 250 N at room temperature. The stress–strain curves of the polymer films were plotted to estimate the films' strength and toughness variations.

3. Results and Discussion

3.1. Effect of αMSD on the Physicochemical Properties of Polymers

Different levels of αMSD were introduced into the emulsion polymerization of (meth) acrylate in order to effectively regulate the physical properties of the resulting polymers. Its effect on average molecular mass, polymerization degree, and monomer conversion is shown in Table 1.

Table 1. Effects of αMSD concentration on average molecular mass, degree of polymerization, and monomer conversion. Note: CTA = chain transfer agent.

Run	CTA	(CTA/M ¹)/%	$M_n/10^4$	\mathcal{D} (M_w/M_n)	\bar{X}_n ²	Conversion/%
1	-	0.0	40.56	3.37	3612	100.0
2	αMSD	0.1	28.58	2.69	2545	97.8
3	αMSD	0.3	12.15	1.96	1082	97.6
4	αMSD	1.0	5.44	1.69	479	88.2
5	αMSD	3.0	1.79	1.61	122	47.3

¹ M is the total weight of methyl methacrylate (MMA) and butyl acrylate (BA); ² \bar{X}_n is the number-average degree of polymerization.

As the addition of αMSD increased from 0% to 0.1%, the number-average molecular weights were evidently decreased from 40.56×10^4 to 28.58×10^4 g/mol, whereas monomer conversion underwent a slight decrease to 97.8%. When αMSD concentration increased from 0.1% to 1%, both molecular weights and monomer conversion were significantly decreased, as the presence of αMSD was able to effectively interfere with the polymerization process. In terms of the dispersity (\mathcal{D}) of the molecular weight, the addition of αMSD contributed to the gradual decrease of the dispersity to nearly 1.60 due to a mathematical artefact in the definition of dispersity [36]. However, despite its efficiency in adjusting molecular weights and \mathcal{D} , only 44.6% monomer conversion was accomplished when the concentration of αMSD was 3%. These results indicate that the utilization of αMSD as a chain transfer agent is effective in the adjustment of the molecular weights and the dispersity \mathcal{D} of synthesized polymers, but a further addition of αMSD might compromise the monomer conversion.

Figure 1 was obtained by plotting the change in logarithm of the concentration of αMSD ($\ln [\alpha\text{MSD}]$) as a function of the logarithm of M_n ($\ln [M_n]$). It showed that the influence of αMSD concentration on M_n was estimated to be $M_n \propto [\alpha\text{MSD}]^{-0.797}$, and the fitting linear expression was $y = 7.458 - 0.797x$ ($R\text{-Square} = 0.983$, $y = \ln [M_n]$, $x = \ln [\alpha\text{MSD}]$). The fitting result quantitatively described the effect of αMD on molecular weight of synthesized polymers, which could be used to estimate the appropriate CTA dosage according to different mass requirements.

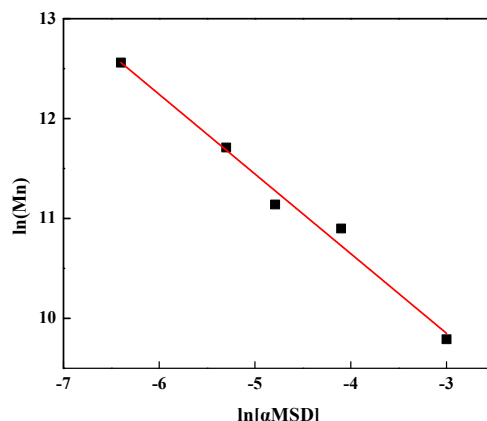


Figure 1. A log–log curve of M_n and α MSD concentration.

In addition, \bar{X}_n in Table 1 was obtained from Equation (1) [37]. As MMA was expected to polymerize first, followed by the polymerization of BA [38], Equation (1) is shown as follows.

$$\bar{X}_n = M_n \left(\frac{x}{m_1} + \frac{1-x}{m_2} \right), \tag{1}$$

$$F_1 = \frac{f_1^0 - (1-C)f_1}{C} \tag{2}$$

$$C = 1 - \left(\frac{f_1}{f_1^0} \right)^\alpha \left(\frac{f_2}{f_2^0} \right)^\beta \left(\frac{f_1^0 - \delta}{f_1 - \delta} \right)^\gamma \tag{3}$$

where x is the mass fraction of MMA in the synthesized copolymers; F_1 as the mole fraction of MMA in the copolymer is calculated by Meyer’s [37] copolymerization equations (Equations (2) and (3)); m_1 and m_2 are the relative molecular masses of MMA and BA, respectively; f_1^0 and f_1 are the mole fractions of MMA in the monomer phase at the beginning and after a certain conversion of the polymerization, respectively; f_2^0 and f_2 are the mole fractions of BA at different stages; C is a monomer conversion; α , β , γ , and δ are coefficients relating to the properties of monomers, which are shown in Table 2.

Table 2. Formulas and values of α , β , γ , and δ .

Coefficients	α	β	γ	δ
Formulas	$\alpha = \frac{r_2}{1-r_2}$	$\beta = \frac{r_1}{1-r_1}$	$\gamma = \frac{1-r_1r_2}{(1-r_1)(1-r_2)}$	$\delta = \frac{1-r_2}{2-r_1-r_2}$
Values	0.52	-2.08	-0.56	-2.44

Note: r_1 and r_2 are reactivity ratios of MMA and BA (shown in Table 4), respectively.

The relative variation tendencies of x and $1-x$ could be seen in Figure 2. As the amounts of initiator and α MSD in the polymerization process were very small, their proportions in the polymer were ignored. It is evident that x increased gradually with increasing amounts of α MSD. This indicated that α MSD affected not only the molecular weights of polymers, but also its composition.

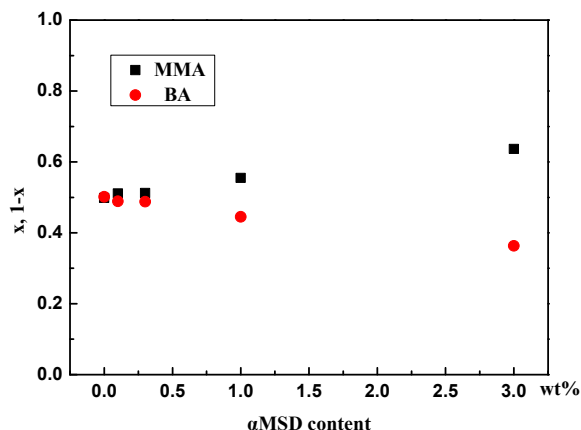


Figure 2. Variation tendencies of the average quality proportion of MMA (x) and BA ($1-x$) in a polymer in the presence of α MSD.

To analyze the potential reason, the reactivity ratios were calculated according to a semi-empirical formula, equation $Q-e$ (Equations (4) and (5)).

$$r_a = \frac{Q_a}{Q_b} \exp[-e_a(e_a - e_b)], \quad (4)$$

$$r_b = \frac{Q_b}{Q_a} \exp[-e_b(e_b - e_a)] \quad (5)$$

where Q and e represent the conjugation degree and polarity of monomer substituents, respectively. r_a and r_b are the reactivity ratios of monomers a and b , respectively. In the case of r_a , a higher value means a larger self-polymerization trend. Alternatively, a lower value indicates a larger copolymerization trend.

During the calculation, the Q and e values for α MSD were estimated using Q and e of alpha methyl styrene (AMS), as α MSD was a dimer of AMS. The specific Q and e values of AMS, MMA, and BA were listed in Table 3, and the calculated reactivity ratios of the three monomers were given in Table 4.

Table 3. $Q-e$ values of alpha methyl styrene (AMS), MMA, and BA.

Monomer	AMS	MMA	BA
Q	0.97	0.74	0.50
e	-0.81	0.40	1.06

Table 4. Reactivity ratios of AMS, MMA, and BA.

MMA/BA	MMA/AMS	AMS/BA
$r_1 = 1.93$	$r_3 = 0.47$	$r_5 = 0.43$
$r_2 = 0.34$	$r_4 = 0.49$	$r_6 = 0.07$

Where r_1 and r_3 are the reactivity ratios for MMA to BA and AMS; r_2 and r_6 are the reactivity ratios for BA to MMA and AMS; and r_4 and r_5 are the reactivity ratios for AMS to MMA and BA, respectively.

As given in Table 4, $r_1 > r_2$ revealed that MMA had a greater polymerization activity than BA, which contributed to a higher x (>0.5) in the early polymerization period. For the sample without α MSD addition (Run 1), BA's mass fraction in the polymers gradually increased up to 50% in the later polymerization period. However, this process would be terminated earlier in the presence of α MSD. Because of the chain transfer reaction of α MSD, the propagation process was terminated significantly earlier with an increase in the amount of α MSD. As a result, the growth of BA's mass fraction in the

polymer was terminated earlier and earlier. Finally, MMA's mass fraction in the polymer increased, whereas the mass fraction of BA was lowered with an increase in the amount of α MSD.

In addition, $r_1 > r_3$ indicated that MMA had a greater tendency to copolymerize with AMS than BA. Similarly, $r_2 > r_6$ indicated that BA tended to copolymerize with AMS rather than MMA. In other words, both MMA and BA were more likely to copolymerize with AMS (α MSD). This could indirectly explain why α MSD effectively controlled the molecular weights of the polymer. For AMS, $r_4 \approx r_5$, there was an almost equal possibility of AMS to copolymerize with MMA or BA.

To compare the regulation reactivity differences of α MSD as a chain transfer agent to MMA and BA more accurately, its transfer coefficients (C_{tr}) to each single monomer were calculated with the following expression (Equation (6)). It was derived by Alfrey [39] for the case of binary copolymerization in the presence of small amounts of CTA, based on the assumption that the only effect of the chain transfer reaction was to terminate one growing molecular chain and start another, i.e., ignoring cases in which a chain transfer also led to the termination of the kinetic chain.

$$K = AC_{tr,a} \frac{[A] + [B]}{[A] + r_a[B]} + BC_{tr,b} \frac{[A] + [B]}{r_b[A] + [B]}, \quad (6)$$

where A and B are mole fractions of monomer A and monomer B, respectively, in the polymer; $[A]$ and $[B]$ are the mole fractions of monomer A and monomer B in the whole monomers; r_a and r_b are the reactivity of the two monomers; and K is the slope of a Mayo-like plot (i.e., $1/\bar{X}_n$ vs. total monomer concentration, Equation (7)) [40,41].

$$\frac{1}{\bar{X}_n} = \frac{1}{\bar{X}_{n,0}} + K \frac{[C]}{[M]}, \quad (7)$$

where $[C]$ and $[M]$ are concentrations of the CTA and whole monomers, respectively; \bar{X}_n is the average degree of polymerization for the polymer at a given $[C]$; and $\bar{X}_{n,0}$ is for the polymer in the absence of CTA.

In this work, MMA and BA were regarded as monomers A and B, respectively, as α MSD was used as the CTA. On the basis of the above analysis, the values of the individual transfer coefficients ($C_{tr,a}$ and $C_{tr,b}$) for a particular monomer ratio were successfully obtained by the two simultaneous equations (Equations (6) and (7)).

Figure 3 displayed the fitting result of the Mayo plot, and K was derived from the slope of the plot: 0.56 (R-Square = 0.986). K remained unchanged as long as the monomer ratio of MMA and BA was a constant. As a consequence, $C_{tr,a}$ and $C_{tr,b}$ could be calculated through Equation (6) by choosing any two runs (including α MSD) in Table 1, such as Run 2 and Run 4, and the result was shown in Table 5.

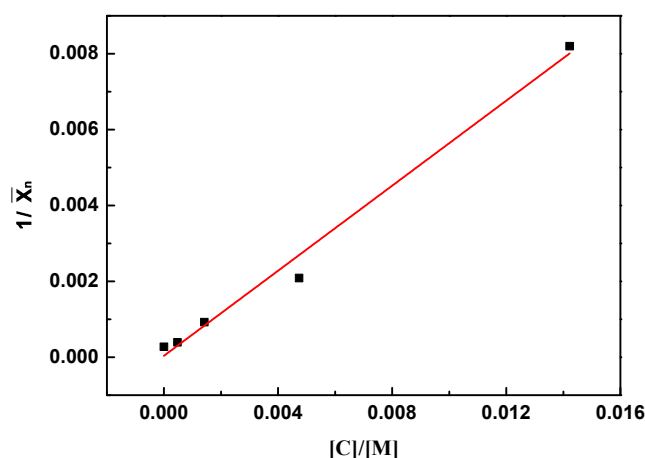


Figure 3. Mayo plot of $1/\bar{X}_n$ vs. total monomer concentration for MMA–BA copolymerization in the presence of α MSD.

Table 5. Transfer coefficients (C_{tr}) measured for α MSD.

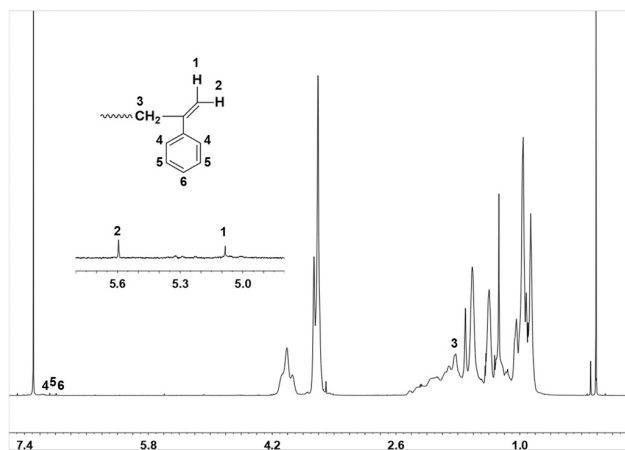
Monomer	CTA	C_{tr}	Reference
MMA	α MSD	0.62	39
BA	α MSD	0.47	39
MMA	α MSD	2.12	<i>Q-e</i>
BA	α MSD	14.28	<i>Q-e</i>

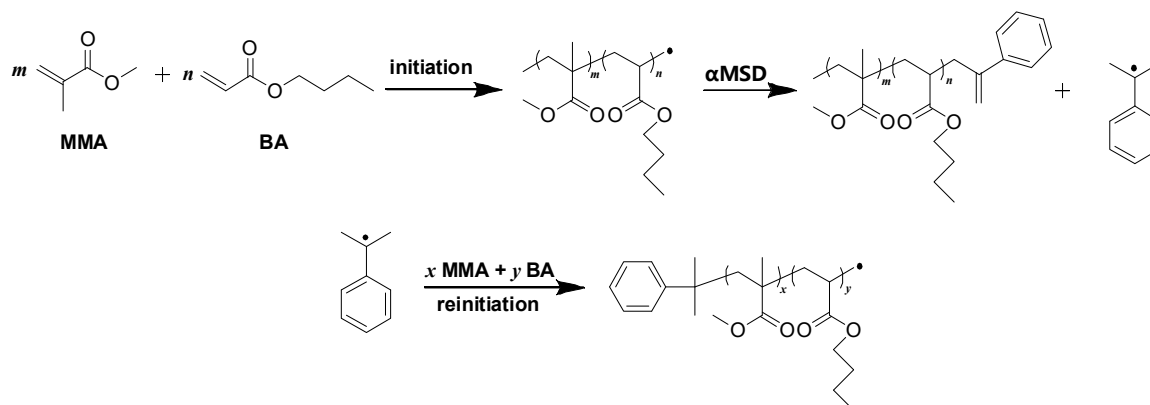
If this polymerization system was treated as a terpolymerization of MMA, BA, and α MSD, the two C_{tr} s of α MSD could be calculated by the reactivity ratios of the three monomers on the basis of *Q-e* values. According to the definition of C_{tr} , the C_{tr} s values of α MSD should be kinetically equivalent to the reciprocals of the reactivity ratios of any two monomers. The calculation results were shown in Table 5.

As shown above, the C_{tr} s values of α MSD determined by different methods were obviously different. $C_{tr,MMA}$ and $C_{tr,BA}$ were 0.62 and 0.47 according to Alfrey's theory, respectively. However, when using *Q-e* method, the former was 2.12 and the latter was increased to 14.28. The difference could be explained from two aspects: First, the C_{tr} calculations based on the *Q-e* method utilized AMS's reactivity ratios to represent α MSD's. Nevertheless, as a dimer of AMS, α MSD's structure was more complex than AMS, and the former had more steric effects when it reacted with other monomers. Thus, their reactivity ratios as well as C_{tr} s should be different. Second, there were some inherent errors in calculating the reactivity ratios using the *Q-e* method.

In contrast to the *Q-e* method, the substitution of AMS for α MSD was avoided in Alfrey's theory, so the C_{tr} s values of α MSD should be more accurate. In addition, the almost same values of $C_{tr,MMA}$ and $C_{tr,BA}$ indicated that α MSD has almost same chain transfer possibilities with both MMA and BA, which was consistent with the above analysis of reactivity ratios in Table 4.

As described above, few studies have been conducted to use α MSD as a chain transfer agent in the emulsion polymerization. Therefore, we have used NMR analysis to reveal its potential mechanism. In the polymerization process, chain propagation would be terminated by the irreversible AFCT agent. Therefore, a part of the polymer's terminal structures consists of the AFCT agent. On this basis, the mechanism for α MSD could be revealed by a polymer terminal structure analysis. The 1H NMR analysis of the resulting polymer using 1% α MSD showed that two signals of similar intensities at approximately 5.0, 5.1, and 5.6 ppm were observed as the characteristic peaks of the two syntonic hydrogen atoms of the terminal double bonds (Figure 4). Moreover, multiple signals at ~ 7.0 ppm were present, which were ascribed to the substituted benzene ring from the α MSD. Accordingly, these results confirmed that emulsion polymerization of acrylates using α MSD as a chain transfer agent followed Yasummasa's mechanism. The detailed regulation mechanism is illustrated in Scheme 4.

**Figure 4.** 1H NMR spectrum of the resulting polymer in the presence of α MSD (content: 1%).



Scheme 4. Chain transfer mechanism of α MSD in MMA and BA emulsion copolymerization.

3.2. Effect of α MSD on the Polymerization Rate

As α MSD has an obvious influence on polymer molecular weights, it was necessary to study if its presence would also affect the polymerization rate (R_p). In the emulsion polymerization, the constant speed stage was typically used as the indicator of total polymerization rate, and it could be calculated from the conversion–time curve. Figure 5 showed the monomer conversion versus reaction time in the presence of α MSD at various concentrations. The slopes of the curves directly reflected R_p . It was clear that the presence of α MSD could decrease the R_p as compared to samples without α MSD. Moreover, as the increase in the quantities of α MSD, R_p was decreased more significantly. For example, the monomer conversion only reached 0.4 after 250 min when 3% of α MSD was added, whereas its conversion approached 100% without α MSD addition. Furthermore, the effect of α MSD concentration ($[\alpha\text{MSD}]$) on R_p was further correlated via constructing a log–log plot of R_p and $[\alpha\text{MSD}]$, as shown in Figure 6. As expected, the result was quantitatively estimated to be $R_p \propto [\alpha\text{MSD}]^{-0.945}$ (R-Square = 0.905).

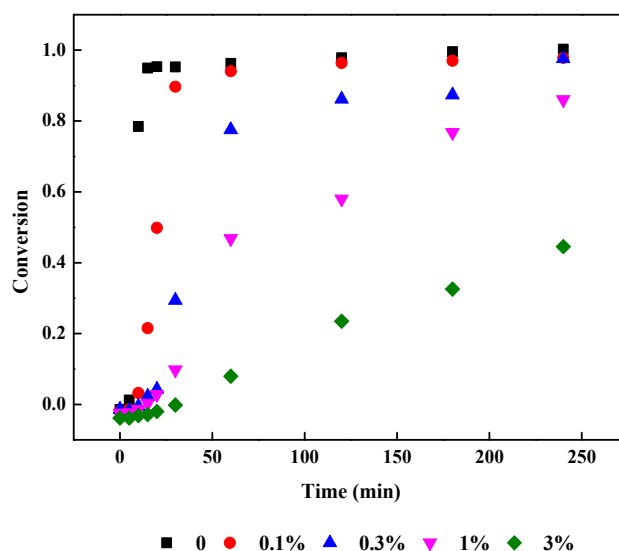


Figure 5. Monomer conversion as a function of reaction time at various molar ratios between α MSD and acrylate monomers (see Table 1).

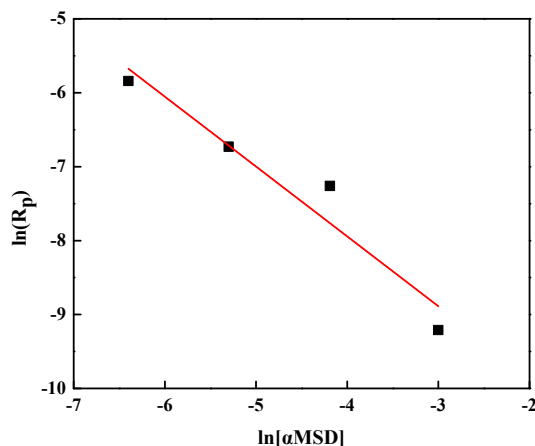


Figure 6. Rate of polymerization as a function of various α MSD concentrations. Slope of linear fit = -0.945 (R -Square = 0.905).

The potential reasons for the decrease in R_p in the presence of α MSD may be explained from two aspects. First of all, the overall rate constant of the scission process of the leaving group may be lower than propagation [20]. The efficient transfer reaction of an irreversible AFCT agent required that transitional radicals, created by the addition reaction of the irreversible AFCT agent and chains radicals, could easily fragment to generate new radicals to reinitiate the polymerization process. As a result, retardation would happen. In fact, the novel radical (isopropyl benzene radical, seen in Scheme 4) in this paper, had less access to reinitiate polymerization than the primary radical (sulfate radical anion) due to its steric hindrance. Thus, the macroscopic reaction rate decreased. Second, radicals derived from both the initiator and leaving groups might escape from micelles or latex particles (desorption) and then be terminated with radicals in either the water phase or polymer particle (reabsorption). This desorption phenomenon had been successfully verified in the emulsion polymerization, and the related theoretical model had been previously established [42–44]. The sulfate radical anion is more hydrophilic than the isopropyl benzene radical. As a result, the desorption number of the former was much greater than latter, and the latter tended to stay in the original particles. This led to serious loss of the high-active free radicals, and in addition, the remaining free radicals in the latex particles were not active enough, which further exacerbated the decline in R_p .

3.3. Effect of α MSD Particle Size and Relevant Parameters

The influence of α MSD concentration on latex particle size (d_p), its distribution (PDI), and particle number (N_c) were also explored, and the results were shown in Table 6. The particle number of the resulting emulsion was calculated using an Equation (8).

$$N_c = \frac{6m}{\pi\rho d_p^3} \times 10^{21}, \quad (8)$$

where m is the solid content of the dispersed phase (containing monomer and polymer at a given conversion and expressed in g/mL^{-1}), and ρ represents the particle density.

As shown in Table 6, d_p declined from 109.38 to 46.88 nm as α MSD dosage was varied from 0% to 3%, whereas N_c was enhanced from 1.67×10^{17} to $20.79 \times 10^{17} \text{ mL}^{-1}$. Moreover, PDI started to dramatically increase when the α MSD dosage was higher than 1%.

According to recent reports [45,46], the exit and entry rates of radicals and monomers into particles have strong effects on miniemulsion polymerization kinetics. In this study, isopropyl benzene radicals derived from α MSD increased the whole radical concentration in the particles, which contributed to the greater desorption of sulfate radical anions. Thus, these sulfate radical anions were resorbed by other micelles, and more micelles could be transformed into polymer particles. This explained the

increase in N_c and the decrease in d_p . Generally speaking, the increase in N_c should be accompanied by inhibition of the termination reaction, leading to a higher reaction rate. However, the actual R_p was decreased. In fact, actual variations of N_c and d_p were not necessarily related to R_p . A mass transfer resistance occurred during the transfer process of sulfate radical anions among the micelles, water, and particles. This would counteract the slight increase in R_p caused by the lower degree of termination. As a result, the variations of N_c and d_p failed to improve R_p .

Table 6. Collection of latex particle size (d_p) and its distribution (PDI) and particle number (N_c) with α MSD at different concentrations.

Run	(CTA/M)/%	d_p (nm)	PDI	N_c (10^{17} mL $^{-1}$)
1	0.0	109.38	0.068	1.67
2	0.1	93.75	0.079	2.68
3	0.3	78.15	0.045	4.58
4	1.0	62.50	0.135	9.07
5	3.0	46.88	0.230	20.79

3.4. The Effect of α MSD on Tensile Properties of Polymer Films

The tensile properties (E , σ_p , and ε_b) of the latex films prepared from polyacrylate emulsion at various α MSD concentrations were determined, and the stress–strain curves were shown in Figure 7. The results were summarized in Table 7. As expected, α MSD addition had an impact on the mechanical properties of the latex film. With the increase in α MSD from 0% to 1%, E and σ_p of the resultant films were reduced by nearly 75% and 50%, respectively, whereas ε_b was only slightly affected. Furthermore, the obvious yield point of the resultant polymers gradually became less obvious when the amount of α MSD was above 0.3%, indicating that the polymer films changed from hard to soft [47]. When the amount of α MSD reached to 3%, E and ε_b were only 2.00 and 0.23 MPa, respectively, and ε_b had decreased to 467%. The toughness of the resultant films was significantly decreased, and the film was soft and weak. The decrease in the molecular weights of polymers was the main reason to lead to the poor mechanical properties.

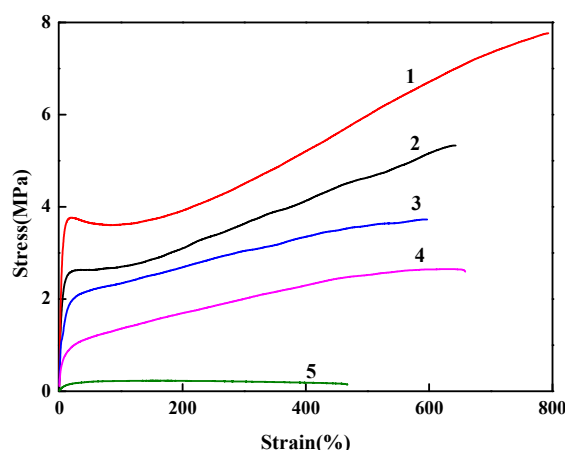


Figure 7. Stress–strain curves of latex films with different α MSD concentrations.

Table 7. Summary of Young's modulus (E), tensile strength (σ_p), and elongation at break (ϵ_b) of films prepared using emulsion polymerization with α MSD as the CTA.

Run	(CTA/M)/%	E (MPa)	σ_p (MPa)	ϵ_b (%)
1	0.0	57.65	5.33	798
2	0.1	52.53	5.06	643
3	0.3	44.28	3.77	564
4	1.0	14.84	2.65	658
5	3.0	2.00	0.23	467

4. Conclusions

In this study, it was shown that α MSD was a highly effective CTA to control the molecular weights in MMA and BA emulsion copolymerization. Molecular masses and their distributions, as well as the mass proportion of MMA in the polymers, were gradually decreased when increasing the dosage of α MSD. Meanwhile, the final monomer conversion was also declined as the α MSD concentration increased above 1%, indicating its apparent inhibition ability of the polymerization. The chain transfer constant of α MSD to MMA was approximately the same with α MSD to BA. The α MSD regulation mechanism was verified by NMR analysis, which was consistent with Yasumasa's theory. In addition, the R_p and d_p of the acrylate latex were decreased as the increase in the dosage of α MSD, while the N_c of the emulsion was increased. Furthermore, the PDI was also affected when α MSD dosage was more than 1%. Finally, the decrease of the tensile properties of the resulting polyacrylate films was mainly due to the reduction in the molecular weights of synthesized polymers after the addition of α MSD.

Author Contributions: Conceptualization, Z.Z. and C.W.; Methodology, Z.Z. and F.C.; Validation, R.C., and F.C.; Formal analysis, Z.Z. and G.F.; Investigation, Z.Z., G.F., and D.Z.; Resources, R.C.; Data curation, C.W. and R.C.; Writing—original draft preparation, Z.Z.; Writing—review and editing, D.Z. and R.C.; Supervision, R.C.; Project administration, R.C.; Funding acquisition, R.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by special funds for basic scientific research operating expenses of central public welfare research institutions of Chinese Academy of Forestry, grant number CAFYBB2018ZB008.

Acknowledgments: This work was financially supported by special funds for basic scientific research operating expenses of central public welfare research institutions of Chinese Academy of Forestry (CAFYBB2018ZB008).

Conflicts of Interest: The authors declare no conflicts of interest.

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