Preparation and Characterization of PMMA and its Derivative *via* RAFT Technique in the Presence of Disulfide as a Source of Chain Transfer Agent

Juan Li, Ting-Ting Jiang, Jiang-Nan Shen* and Hui-Min Ruan

College of Chemical Engineering and Materials of Zhejiang University of Technology Hangzhou, 310014, China

Abstract: Poly(methyl methacrylate) (PMMA) were synthesized by using chain transfer agents(CTA), S-1-Dodecyl-S′-(α,α′-dimethyl-α-acetic acid) trithiocarbonate (MTTCD), S,S′-bis (2-hydroxyethyl-2′-dimethylacrylate) trithiocarbonate (BDATC), 2-cyanoprop-2-yl dithiobenzoate (CPDB) respectively, through the reversible addition fragmentation chain transfer (RAFT) polymerization under a range of synthesis conditions. The results indicated that the structure of the end-group of RAFT agents had significant effects on the ability to control polymerization. Compared with MTTCD and CPDB, BDATC can provide better control over the relative molecular mass, distribution and polymerization of PMMA. The derived well-controlled block copolymer PMMA-b-PDMAEMA and PMMA-b-PDMAEA were also successfully prepared by using N, N-dimethylaminoethy acrylate (DMAEA) or N, N-dimethylaminoethyl methacrylate (DMAEMA) as the second monomer. The chemical composition and structure of the products were characterized by FTIR, ^{1}HNMR, XRD and DSC. CO_2 and N_2 permeation performance of the PMMA-b-PDMAEA/PS composite membranes were tested at different pressure. The results showed that the resulted composited membrane had a CO_2 permeation rate of 3.68×10^{-5}cm^3 (STP) cm^{-2}s^{-1}cmHg^{-1}, a N_2 permeation rate of 1.78×10^{-7} cm^3 (STP) cm^{-2}s^{-1}cmHg^{-1} and an ideal CO_2/ N_2 selectivity of 206.6 at a feed gas pressure of 7.6 cmHg and 30 °C.

Keywords: Reversible addition fragmentation chain transfer (RAFT)polymerization, Disulfide compounds, Theoretical molecular weight, PMMA-b-PDMAEMA, PMMA- b-PDMAEA.

1. INTRODUCTION

Facilitated transport membranes for gas separation have attracted the attention of many researchers, due to their very high permselectivity compared with conventional polymeric membranes [1]. Moreover, they involve a carrier mediated transport in addition to permeate physical dissolution and diffusion. In recent years, fixed carrier membranes for CO_2 separation with facilitated transport groups of amine moieties have been investigated extensively [2-4]. Kima *et al*. [5] developed a new cation-exchange polysaccharide membrane containing a diamine complexing agent for CO_2 facilitated transport. The effect of amino acids such as asparagine, valine, glutamic acid and glycine on silver ion activity as an olefin carrier in membrane consisting of silver ions dissolved in poly(2-ethyl-2-oxazoline) (POZ) has been investigated [6]. Novel fixed carrier composite membranes were developed by interfacial polymerization with water-soluble trimethylene tetramine (TETA) and hexane-soluble trimesoyl chloride (TMC) on polyethersulfone (PES) supports [7]. Wang *et al*. [8-10] prepared a series of facilitated transport membranes through various methods. For example, a membrane material containing facilitated transport groups for carbon dioxide through the hydrolysis of polyvinylpyrrolidone (PVP) obtained by radical polymerization. His group also first reported N-vinyl-γ-sodium aminobutyrate-sodium acrylate copolymer (VSA-SA) using free radical polymerization. Shen [11] prepared a facilitated transport membrane based on the solid polymer electrolytes of poly(vinyl alcohol)-Co^{2+} (PVA-Co^{2+}) blends. Poly(acrylic acid) (PAA)/poly(vinyl alcohol) (PVA) membrane was prepared for the facilitated transport of CO_2. The carrier of CO_2 was monoprotonated ethylenedi-amine which was introduced in the membrane by ion exchange [12]. However, RAFT process to prepare facilitated transport membrane materials containing groups of amine moieties has seldom been reported in the past work.

The chemical versatility by controlling the agents during the RAFT process makes RAFT-based procedures highly attractive for the preparation of well-defined polymers with specific polymer architectures [13-15]. The first reversible addition fragmentation chain transfer (RAFT) polymerization was reported by Rizzardo in 1998 [16]. Up to now, the RAFT polymerization has been successfully applied to many monomers including functional and water-soluble monomers [17-19]. RAFT polymerization consists in the introduction of a small amount of thiocarbonylthio compound as the chain transfer agent (CTA) into a classical free radical polymerization system. RAFT agents are mainly dithioester, 2, 3-xanthate,

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*Address corresponding to this author at the College of Chemical Engineering and Materials of Zhejiang University of Technology Hangzhou, 310014, China; Tel: +86 571 88320711; Fax: +86 571 88320711; E-mail: shenjn@zjut.edu.cn

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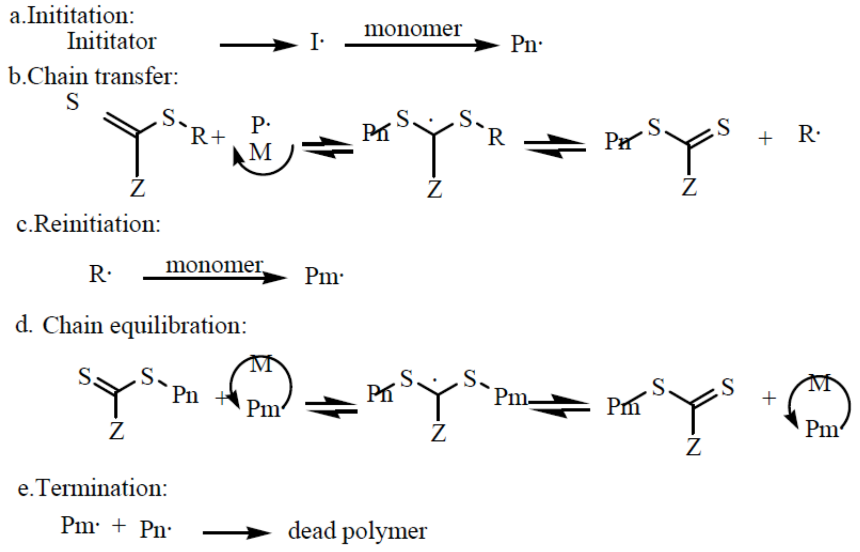
trithiocarbonate [20] and dithiocarbamate [21-24]. Rizzado and other researchers [25-27] have reported that the RAFT polymerization under a particular set of reaction conditions depending on the nature of the Z and R groups of RAFT agents. With the appropriate choice of CTA/monomer system and reaction conditions, the well-defined polymers with predictable molecular weights, low polydispersity indices (PDIs), and precisely controlled architectures can be produced [28]. The mechanism of the RAFT process is shown in Scheme **1**. RAFT polymerization comprises five steps: initiation, transfer, reinitiation, chain equilibration, termination. Initiation and termination occur as in conventional radical polymerization. In the early stages of the polymerization, addition of a propagating radical ($P_n\cdot$) to the thiocarbonylthio compound [RSC(Z)=S(1)] followed by fragmentation of the intermediate radical provides a polymeric thiocarbonylthio compound [P_nSC(Z)=S (3)] and a new radical(R·). Reaction of this radical (R·) with monomer forms a new propagating radical($P_m\cdot$). Rapid equilibrium between the active propagating radicals and the dormant polymeric thiocarbonylthio compounds(3) provides equal probability for all chains to grow and allows for the production of narrow polydispersity polymers. Block copolymerization of a functional monomer with an existing polymer offers an effective approach to incorporating new properties into the parent polymer, while retaining the desirable properties of the parent polymer. MMA, DMAEMA and DMAEA are potential monomers that can be used to prepare membranes for CO_2 separation.

In this article, the controlled/living radical polymerization of MMA with MTTCD, BDATC, CPDB (Scheme **2**) as a RAFT agent and AIBN as an initiator in a 1, 4-dixoane solution was reported. Well-defined PMMA homopolymers, PMMA-b-PDMAEMA and PMMA-b-PDMAEA block polymers were successfully synthesized. The chemical composition and structure were analyzed by FTIR, ^{1}HNMR, XRD and DSC, the molecular weight and polydispersity index were analyzed by GPC. The effects of AIBN/CTA dosage and monomer/CTA dosage on the polymerization kinetics were discussed.

2. EXPERIMENTAL

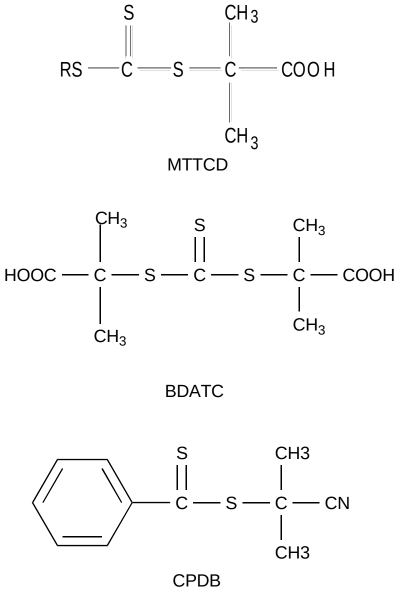
2.1. Materials

MMA, DMAEMA and DMAEA were purified by being reduced pressure to remove inhibitor. These chemicals (analytical reagents) were purchased from Shanghai Chemical Reagent Co., Ltd., China. 1, 4-dioxane was distilled from $LiAlH_4$ (110 °C). 2, 2′-Azo-bis(isobutyronitrile) (AIBN) (Fluka, 98 %) was purified by re-crystallization from ethanol at 40 °C, dried at room temperature in vacuum, and stored in a refrigerator at -15 °C. All other chemicals used in the experiments were commercially analytical grade. Disulfide compounds were prepared according to the method described in documents. Their molecular structures were shown in Scheme **2**. MTTCD was synthesized according to the methods reported in the literature [29]. ^{1}HNMR($CDCl_3$): 1.94 ppm (s, 6H, m-$C(CH_3)_2$), 7.40 ppm (m, 2H, m-ArH), 7.58 ppm (m, 1H, m-ArH), 7.91 ppm (m, 1H, o-ArH). BDATC was synthesized according to the methods reported in the literature [29], IR (KBr, cm^{-1}): 1700, 1060;



Scheme 1: Mechanism of the RAFT process.

^{1}HNMR($CDCl_3$, δ): 1.59, 11.0. CPDB was synthesized according to the methods reported in the literature [30], ^{1}HNMR($CDCl_3$): 1.94 ppm (s, 6H, m-$C(CH_3)_2$), 7.40 ppm (m, 2H, m-ArH), 7.58 ppm (m, 1H, m -ArH), 7.91 ppm (m, 1H, o-ArH).



Scheme 2: Chemical structures of MTTCD, BDATC, CPDB.

The permeation testing set-up used were similar to reported previously. The effective area of the tested composite membrane is 19.6 cm^2. The obtained membrane was tested by feed gas which was pure gas of CO_2 and N_2. The permeation rate of the gas was calculated from the flow rate of H_2 which is the sweep gas and the integral area of the penetrate gas, CO_2 and N_2, from the gas chromatograph with a thermal conductivity detector. The permeation rate and the selectivity are given by $R_i=N_i/\Delta p_i$, $S_{CO2/N2}=R_{CO2}/R_{N2}$.

Where N_i is the permeation flux of permeate gas, Δp_i is the trans-membrane partial pressure difference. R_{CO2}, R_{N2} are the permeation rate of CO_2 and N_2, respectively.

2.2. Polymerization

2.2.1. RAFT Polymerization of MMA

A typical polymerization procedure is as follows. Schlenk polymerization tubes were filled with MMA, AIBN, MTTCD or BDATC or CPDB, and 1, 4-dixoane were degassed by three freeze-pump-thaw cycles, then charged with nitrogen and sealed. The polymerization tubes were heated at 70 ^oC in a thermostated oil bath. After a predetermined time, the content was stopped by cooling the solution in ice water and diluted with THF. The polymer solution was poured into a large excess of petroleum ether to precipitate PMMA homopolymer. The viscous polymer was dried under the condition of vacuum to a constant weight. The monomer conversions were determined gravimetrically. The molecular weights increased linearly with monomer conversion and were close to the theoretical molecular weights which were obtained from following equation:

$$M_{n,th} = M_{n,Raft} + \frac{[MMA]_0 \cdot M_0 \cdot x}{[RAFT]_0} \tag{1}$$

where $[MMA]_0$ and $[RAFT]_0$ are the starting concentrations of the MMA and the RAFT agent, respectively, x is the fractional conversion, and M_0 is the molar mass of the MMA. $M_{n,raft}$ is the molar mass of the RAFT agent.

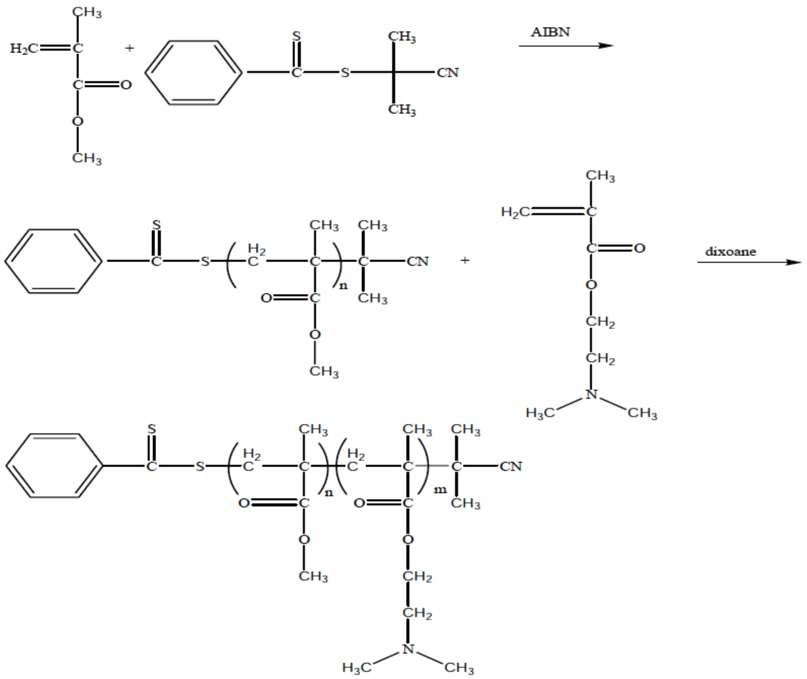
2.2.2. Polymerization of DMAEMA and DMAEA with PMMA-CTA as a Macro-RAFT Agent

The RAFT polymerizations of DMAEMA and DMAEA were carried out with the same procedure mentioned previously. PMMA-CTA (0.54 g, 0.01 mmol), DMAEMA (0.78605 g, 500 mmol), and AIBN (0.54 mg, 0.0033 mmol) were dissolved in 1,4-dioxane in a flask. The solution was degassed by three freeze-vacuum-thaw cycles. The block copolymerization was carried out at 70 ^oC for 10 h and stopped by cooling the solution in iced water. The polymer solution was poured into a large excess of petroleum ether to precipitate PMMA-b-PDMAEMA block copolymer. The block polymer was dried under the condition of vacuum to a constant weight. The synthetic route for PMMA-b-PDMAEMA in presence of CPDB is shown in Scheme **3**.

From Scheme **3**, we can see that firstly macromolecules chain transfer agents poly(methyl methacrylate) (PMMA-CTA) were synthesized through RAFT polymerization by using CPDB as the chain transfer agents and MMA as the first monomer. Then to demonstrate the living character of this polymerization system, PMMA chain was subsequently extended with DMAEMA to yield a block copolymer and lastly the derived well-controlled block copolymer PMMA-b-PDMAEA were successfully prepared.

2.3. Characterization

The chemical structure of the PMMA, PMMA-b-PDMAEMA and PMMA-b-PDMAEA polymer were studied by FT-IR spectroscopy on a Nicolet 6700 FT-IR spectrophotometer (Thermo, Inc., America), with the



Scheme 3: The synthetic route for PMMA-b-PDMAEMA in presence of CPDB.

polymer samples dispersed in KBr pellets. The copolymer compositions were determined by NMR spectroscopy. ^{1}HNMR measurements were performed on a UNITY-plus 400 M nuclear magnetic resonance spectrometer(Varian, Inc., America) using $CDCl_3$ as the solvent. The thermal behavior was analyzed by differential scanning calorimetry on a NETZSCH DSC 200 (Netzsch, Inc., Germany). The DSC scanning was performed at a heating rate of 10 ^{o}C/min under inert atmospheres. XRD was used to test the crystalline of the polymers on a X′ pert Pro X-ray diffraction(PANalytical, Netherlands). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (M_w/M_n) of the polymers were estimated by gel permeation chromatograph (GPC)/size exclusion chromatography (SEC) at 30 ^{o}C with a Waters chromatography, Inc. (Milford) system equipped with an isocratic pump model 1525, a refractometer model 2414. THF was used as the mobile phase at a flow rate of 1.0 mL/min.

2.4. Membrane Preparation and Performance

Membranes for separation tests were prepared by solution casting and the solvent evaporation technique. PMMA-b-PDMAEA aqueous solutions of 8wt% were prepared. Then the solution was filtered to remove any undissolved suspend matters. The cast solution used for casting the membranes was de-foamed in the vacuum. The membrane was prepared by casting the polymer solution on polysulfone ultrafiltration membrane, the PSF support membrane was previously rinsed with dilute NaOH solution and flushed with deionized water to remove any possible contaminants from supplier before use, followed by evaporation at room temperature for more than 24 hours.

The permeation testing set-up used were similar to reported previously. The effective area of the tested composite membrane is 19.6 cm^2. The obtained membrane was tested by feed gas which was pure gas of CO_2 and N_2. The permeation rate of the gas was calculated from the flow rate of H_2 which is the sweep gas and the integral area of the penetrate gas, CO_2 and N_2, from the gas chromatograph with a thermal conductivity detector. The permeation rate and the selectivity are given by $R_i=N_i/\Delta pi$, $S_{CO2/N2}=R_{CO2/RN2}$.Where N_i is the permeation flux of permeate gas, Δp_i is the trans-membrane partial pressure difference. R_{CO2}, R_{N2} are the permeation rate of CO_2 and N_2, respectively.

3. RESULTS AND DISCUSSIONS

3.1. RAFT Polymerization of MMA Using Disulfide Compounds as a Source of CTA

According to the RAFT polymerization mechanism, the success of the RAFT polymerization of a particular monomer depends on R group's structure of a CTA [31]. The RAFT polymerizations of MMA with MTTCD, DBTTC and CPDB as RAFT agent and AIBN initiator,

Table 1: RAFT Polymerization Results of MMA in the Presence of MTTCD, BDATC, CPDB

Numbers	RAFT agents	Time(h)	M/R/I	Conversion	M_n^a (GPC)	M_n^b (theoretical)	M_w/M_n
1	MTTCD	10	150:3:1	59.5%	8052	3338	1.77
2	MTTCD	10	300:3:1	75.2%	11463	7883	1.66
3	BDATC	10	300:3:1	50.0%	20551	5282	1.43
4	BDATC	6	300:3:1	21.7%	16903	2167	1.33
5	BDATC	5	300:3:1	35.7%	8196	3852	1.26
6	BDATC	5	600:3:1	44.4%	13933	9162	1.30
7	BDATC	3	600:3:1	11.3%	7680	2542	1.27
8	BDATC	3	50:3:1	15.2%	4836	532	1.25
9	CPDB	10	900:3:1	19.9%	53539	6214	1.67
10	CPDB	10	1500:3:1	49.2%	96592	24827	1.66

[a]Mn value measured by GPC is larger than the true value as reported. [b]computed by equation:$M_n(th)=M_{RAFT} + n \cdot Conv \cdot M_{MMA}$. Reaction temperature 70°C.

respectively, were carried out. The conditions and results are listed in Table **1**. When MMA was polymerized in the absence of MTTCD and CPDB (entry 1-2, 9-10). The resultant PMMA has a polydispersity indice (PDI) > 1.50. The reason for this phenomenon maybe not only the CTA, but also the chain transfer ability which doesn't match with the activity of monomer. These PMMA chains are inactive macro RAFT agents which may also come from the polymerization process or from suboptimal purification. However, the polymerization of MMA in the presence of BDATC (entries 3-8 in Table **1**) showed that the relative molecular mass of polymer was controllable. The polymer obtained was narrow in polydispersity index (< 1.5) and low monomer conversions. The polymerization is controlled for low ratios ([MMA]:[CTA]). At higher ratios, the polymerization is plagued by transferring to solvent. The contribution of transferring to solvent could have been attenuated by polymerizing at higher monomer concentration, but at such concentration, the increase of viscosity will result in a loss of control and broad PDIs [32]. On the other hand, in any [MMA]:[CTA] ratios, the polymer molecular weight is above the theoretical molecular weight, because the first transferring between CTA and a propagating radical is less efficient than the subsequent transferring between a dormant chain and a propagating radical [33].

3.2. Polymerization of MMA at Different Temperatures

The effect of the polymerization temperature on the rate of the RAFT solution polymerization of MMA with AIBN as an initiator and BDATC as a RAFT agent was investigated, and the results are shown in Figure **1** and Table **2**. As shown in Figure **1**, the corresponding plots of $\ln([M]_0/[M])$ versus the polymerization time (where $[M]_0$ is the initial monomer concentration and [M] is the monomer concentration) are nearly linear for all the polymerization temperatures (70 °C and 80 °C), which indicates that the radical concentrations were constant during the reactions. It also can be seen that the polymerization rate increased significantly with increasing polymerization temperature, which can be attributed to the fact that AIBN decomposes more quickly at a higher polymerization temperature than at a lower one. As shown in Table **2**, The molecular weight distributions are relatively narrow (all of M_w/M_n < 1.31) at different temperatures. However, the value of Mn(GPC) decreases as the increase in temperature

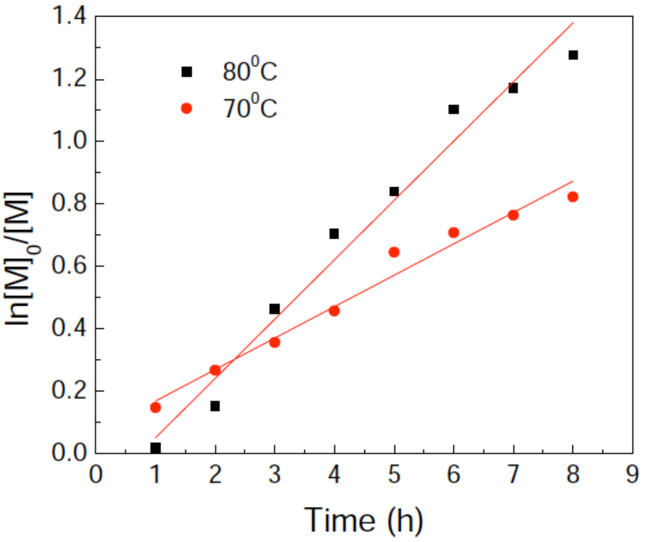


Figure 1: The pseudo-first-order kinetic plots(circles) for the polymerization of MMA with BDATC in the presence of AIBN in 1,4-dixoane at 70 °C, 80 °C using a $[MMA]_0/ [BDATC]_0/ [AIBN]_0=300:1:0.33$.

Table 2: The polymerization of MMA at Different Reaction Temperature, $[MMA]_0$ /$[BDATC]_0$ / $[AIBN]_0$=50:3:1

Numbers	Temperature (°C)	Time (h)	M_n (GPC)	$M_{n,th}$ (theoretical)	M_w/M_n
1	65	3	4625	449	1.31
2	70	3	4836	532	1.25
3	75	3	4595	614	1.27
4	80	3	4483	1024	1.30

from 70 °C to 80 °C, which is not agreement with the traditional theory .The reason maybe is the concentration of free radicals and free radical chains is very high in the polymerization system when at the high temperature, but the reaction time is short (only 3h)so that there is no enough time for chains to propagate.

3.3. Polymerization of MMA in the Presence of MTTCD

Figures **2** and **3** show the plot of monomer conversion and $\ln([M]_0/[M])$ versus reaction time for polymerization of MMA by RAFT using MTTCD as transfer agent in 1, 4-dixoane at 65 °C. The plot is approximately linear, which indicates that the system is in a stationary state with respect to the ratio (Rp/[M] = Kp[P•]) [34].

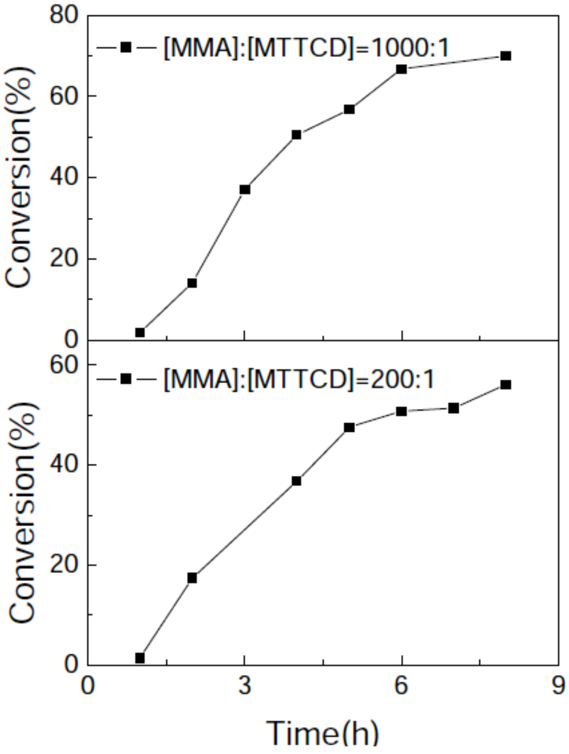


Figure 2: Conversion as a function of reaction time for polymerization of MMA by RAFT at 65 °C, [MMA]=3.3mol/L, [MTTCD]:[AIBN]=3:1.

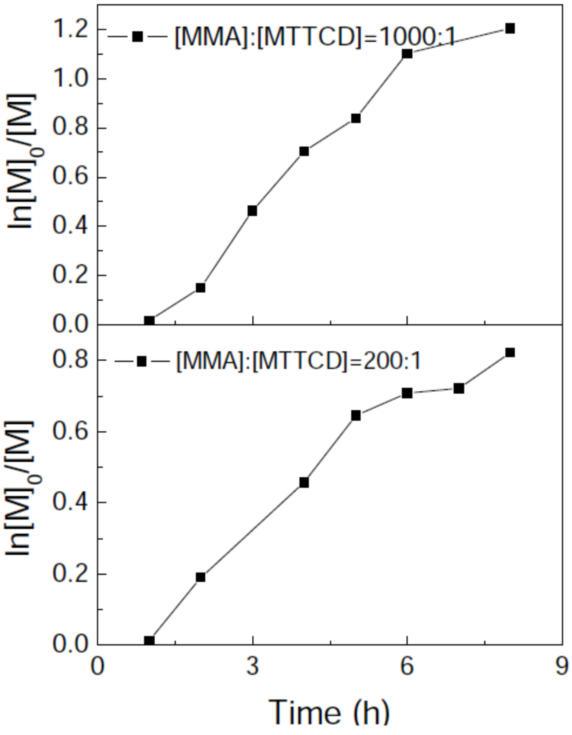


Figure 3: First-order kinetic plot of $\ln([M]_0/[M])$ as a function of reaction time for polymerization of MMA by RAFT at 65°C, [MMA]=3.3mol/L, [MTTCD]:[AIBN]=3:1.

3.4. Polymerization of MMA in the Presence of CPDB

The polymerization of MMA with AIBN in the presence of CPDB in 1, 4-dixoane at 65 °C was investigated at a monomer/CTA/initiator molar ratio, $[MMA]_0/[CPDB]_0/[AIBN]_0$ = 500:1:0.33. The time-conversion and the pseudo first-order kinetic plots are shown in Figure **4**. The linearity of the pseudo first-order kinetic plot suggests that there is a constant radical concentration throughout the RAFT polymerization and the polymerization occurs in a controlled manner.

3.5. Synthesis of PMMA-b-PDMAEMA and PMMA-b-PDMAEA Block Polymers

With the polymer capped by the dithioester moiety, the PMMA-b-PDMAEMA and PMMA-b-PDMAEA

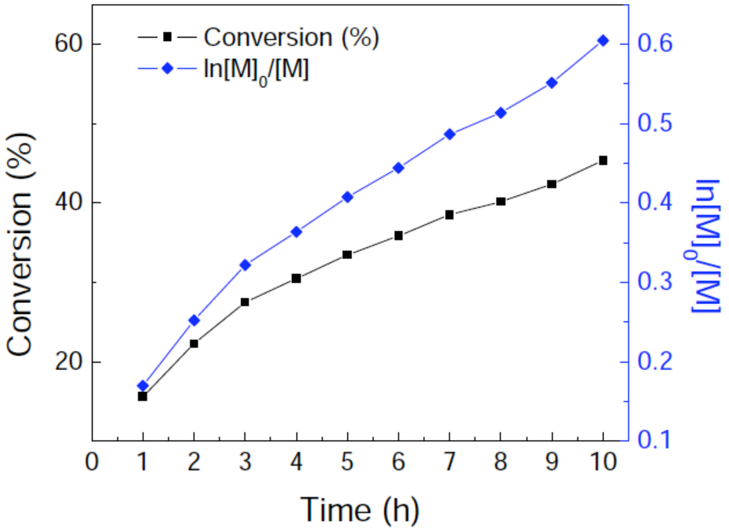


Figure 4: Time-conversion (squares) and The pseudo-first-order kinetic plots(circles) for the polymerization of MMA with CPDB in the presence of AIBN in 1,4-dixoane at 65 °C using a $[MMA]_0$/ $[CPDB]_0$/ $[AIBN]_0$=500:1:0.33.

diblock polymers were synthesized with the original polymers (number-average molecular weight (M_n = 13350) as the macro-RAFT agents with a $[DMAEMA]_0/[PMMA]/[AIBN]_0$ molar ratio and $[DMAEA]_0/[PMMA\text{-}CTA]/[AIBN]_0$ molar ratio(300:3:1, 500:3:1, 900:3:1) in 1, 4-dixoane (monomer/1, 4-dixoane=1:2 v/v) at 70 °C, respectively. The polymerization of all monomers was well-controlled, in good agreement with theoretical molecular weights, and produced low PDI polymers. As an example, the effect of the Macro-RAFT of MMA with AIBN as an initiator and DMAEA as a second monomer was investigated, and the results are shown in Table **3**. The molecular weight distributions are relatively narrow (all of M_w/M_n < 1.3) in all cases, which indicates that the original polymer is active. All these results show that these BDATC is effective controlling agent for the RAFT polymerization of MMA and DMAEA.

3.6. IR Analysis

Figure **5** shows FTIR spectra of block copolymer PMMA-b-PDMAEMA (Spectrum a) and PMMA homopolymer (Spectrum b). As illustrated in Figure **5**, the FTIR spectra of the PMMA contains the characteristic band for C=O stretching (*v* = 1730.8 cm^{-1}) and C-O stretching (*v* = 1149.0 cm^{-1}). On the other hand, there are three strong absorption peaks around 2900 cm^{-1} attributed to the stretching vibrations of -CH_3 and -CH_2- groups. The absorption peak at 1064.5 cm^{-1} is the typical stretching vibrations of C=S groups in CTA. The result of FT-TR indicates that PMMA is obtained and can be reacted as Macro-RAFT agent. The FTIR spectra of the PMMA-b-PDMAEMA contains the characteristic band for O-C=O stretching (*v* = 1730.8 cm^{-1}), associated with the -COOC groups of the blocked PMMA side chains, otherwise, it has been found that the absorption peak of tertiary amine at 1102 cm^{-1}.

3.7. ^{1}H NMR Characterization

The ^{1}HNMR spectrums of homopolymer PMMA and copolymer PMMA-b-PDMAEMA are shown in Figure **6**. It is evident that the peaks appear between 7.27 and 7.90 ppm which are assigned to the protons of phenyl. Some peaks between 1.33 and 2.12 ppm are relative to the methylene protons of main chains. The two singals around 1.0 ppm are assigned to the methyl group. The signal at 3.6 ppm corresponds to the methyl protons of

Table 3: RAFT polymerization Results of DMAEA in the Presence of PMMA-CTA

Reaction condition	PMMA-RAFT (g)	DMAEA (ml)	Initiator AIBN(g)	Solvent 1,4-dioxane(ml)	[M]:[PMM-RAFT]:[AIBN]	[M]:Solvent	M_w/M_n
70 °C, 10h	0.628	0.5	0.00164	25	300:3:1	1:2	1.22
	0.628	0.833	0.00164	25	500:3:1	1:2	1.25
	0.628	1.5	0.0667	17.5	900:3:1	1:2	1.24

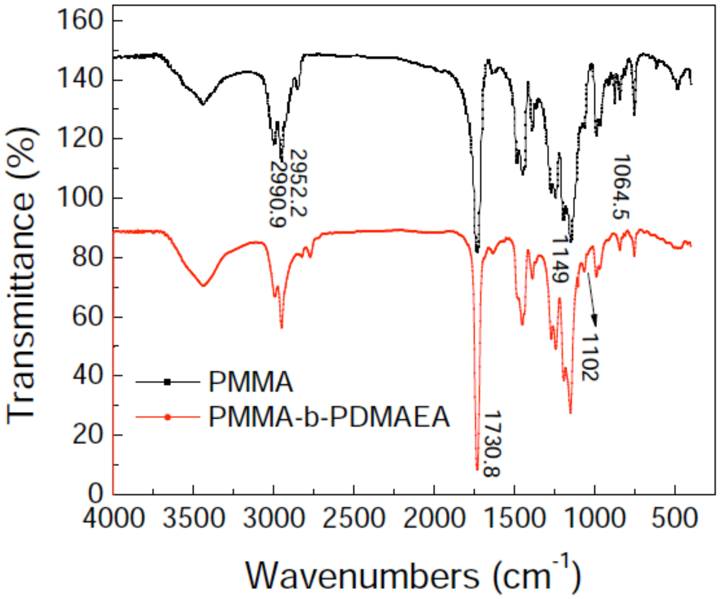
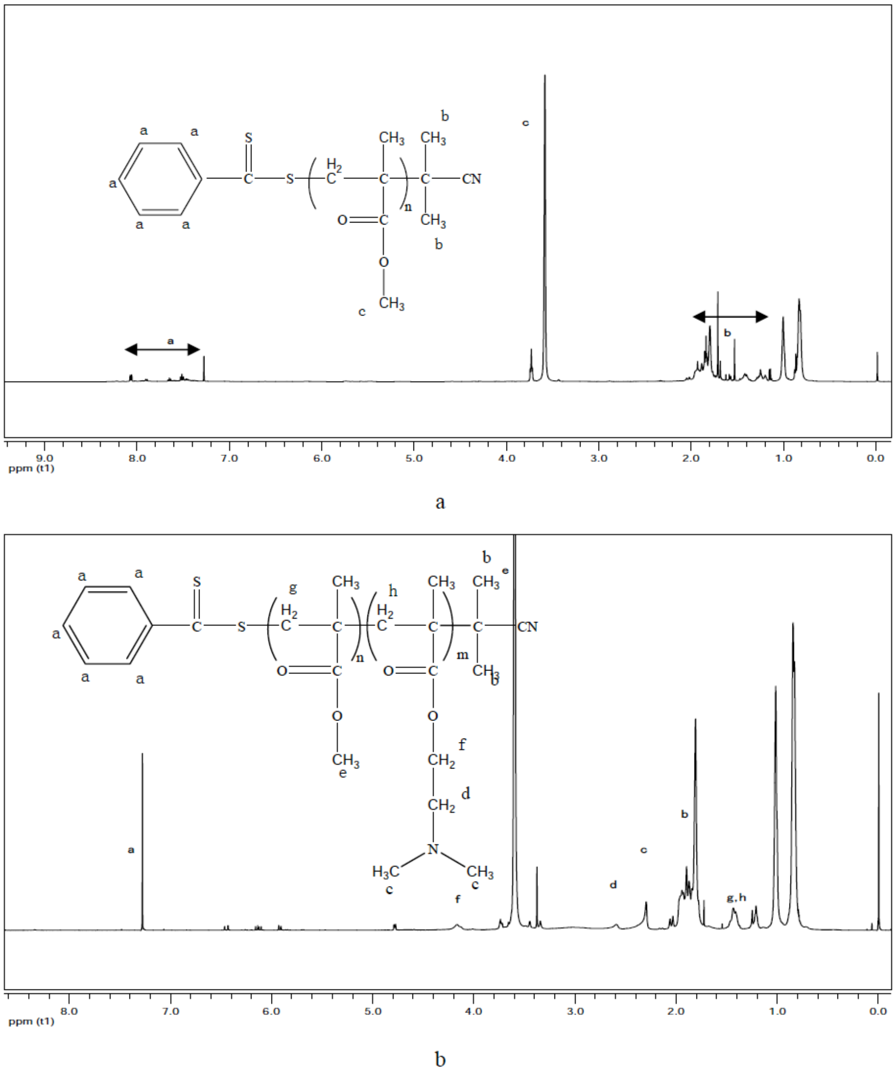


Figure 5: FTIR spectra of PMMA and PMMA-b-PDMAEA.



a

b

Figure 6: ^{1}H NMR spectra of the diblock polymers: (**a**) PMMA-CTA and (**b**) PMMA-b-PDMAEMA.

methoxyl group. The chemical shifts at 2.36 ppm (c) and 4.1 ppm (f) can be assigned, respectively, to the methylene protons (-NCH_2-) and (-OCH_2-) of the PDMAEMA side chain. All of the results indicate that the copolymer is successfully synthesized.

3.8. DSC Analysis

Thermal property of the polymers was evaluated by differential scanning calorimetry (DSC). The DSC heating curves of the homopolymers PMMA, PDMAEMA and copolymer PMMA-b-PDMAEMA were given in Figure **7**. The results showed typical glass transition temperatures (Tg) of homopolymer PMMA and PDMAEMA at 48.4 ^{o}C and 32.6 ^{o}C, respectively. Although PMMA and PDMAEMA are immiscible [35], there is only one glass transition point showed in block copolymer at 33.5 ^{o}C which was between that of precursor homopolymer PMMA and PDMAEMA. The reason may be due to the low molecular weight of PMMA and PDMAEMA in the block copolymer [36]. No obvious phase separation occurs in current block copolymer.

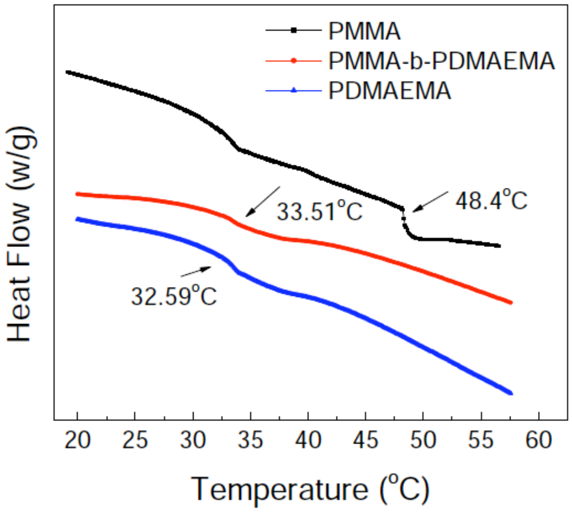


Figure 7: The DSC traces of the PMMA, PMMA-b-PDMAEMA.

3.9. XRD Analysis

XRD traces of the PMMA-CTA and PMMA-b-PDMAEMA are shown in Figure **8**. The diffraction peak of PMMA-CTA and PMMA-b-PDMAEMA are formed by amorphous diffuse peak, which suggesting that they are completely amorphous polymers.

3.9. Size Exclusion Chromatography (SEC)

Molecular weight and PDI measurement methods were carefully assessed because of their critical nature to the rest of this work. SEC traces of the PMMA macro RAFT agent and PMMA-b-PDMAEA block copolymers after dialysis are shown in Figure **9**. DMAEA was polymerized in the presence of a PMMA macro-CTA. A clear shift of the GPC peak toward short elution time indicates that the chain extension has occurred. The SEC chromatogram of the chain extension of PMMA with DMAEA indicates near-quantitative blocking efficiency with the resulted diblocking copolymers having narrow, unimodal molecular weight distributions [37]. The inexistence of a new peak or a shoulder in the GPC curve shows that there is no homo-PDMAEMA.

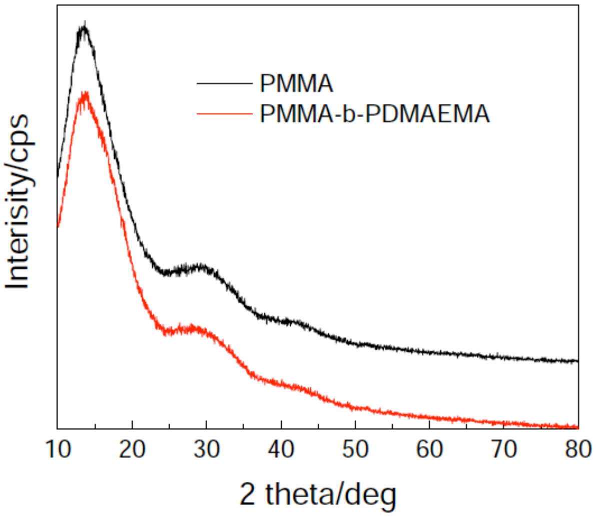


Figure 8: The XRD traces of the PMMA, PMMA-b-PDMAEMA.

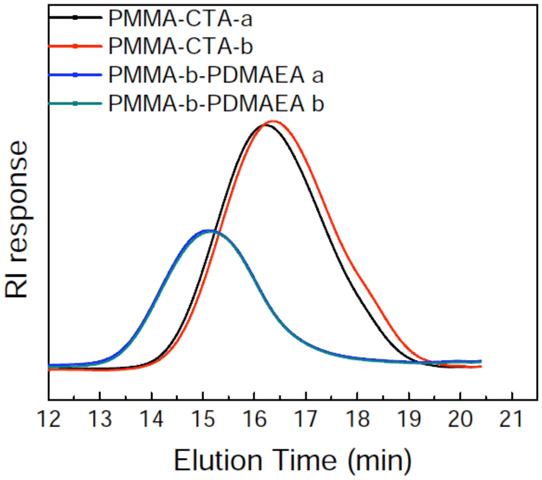
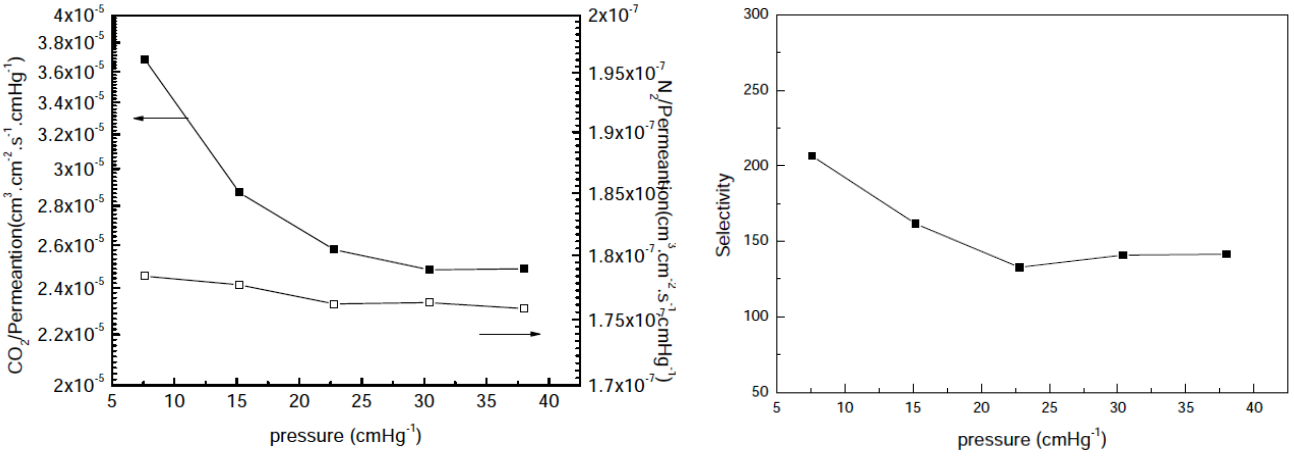


Figure 9: The GPC traces of the PMMA, PMMA-b-PDMAEA.

4. CO_2 SEPARATION PERFORMANCE OF PMMA-B-PDMAEA/PS COMPOSITE MEMBRANES SYNTHESIZED BY RAFT

Figure **10** shows performance of the PMMA-b-PDMAEA/PS composite membrane in different



a **b**

Figure 10: Performance of the PMMA-b-PDMAEMA/PS composite membrane in different pressure (**a**) CO_2 and N_2 permeation rate (**b**) Ideal selectivity of CO_2 over N_2(Test temperature 30 ^oC, pure gas).

pressure (a) CO_2 and N_2 permeation rate (b) selectivity of CO_2 over N_2. The figure shows that the CO_2 gas permeation rate decreases while the feed gas pressure increases. It is due to the increscent pressure increases the concentration of CO_2 in the membrane, which results in facilitated transport reversible reaction. The penetration rate of N_2 changes unobviously when the feed gas pressure changes. This is because N_2 follows the dissolution diffusion mechanism. The resulted composited membrane had a CO_2 permeation rate of 3.68×10^{-5} cm^3 (STP) $cm^{-2}s^{-1}cmHg^{-1}$ and a N_2 permeation rate of 1.78×10^{-7} cm^3 (STP) $cm^{-2}s^{-1}cmHg^{-1}$ and an ideal CO_2/ N_2 selectivity of 206.6 at a feed gas pressure of 7.6 cmHg and 30 ^oC. Further investigation of experimental conditions on membrane performance and membrane stability will be done in our lab.

5. CONCLUSION

The RAFT (co)polymerization of MMA has been successfully carried out in the presence of MTTCD, BDATC and CPDB as the chain transfer agent with the purpose to synthesize PMMA-CTA. The results show that the structure of the end-group of RAFT agents had significant effects on the ability to control polymerization. The polymerization is controlled for low ratios ([MMA]:[CTA]). At higher ratios, the polymerization is plagued by transfer to solvent. BDATC is the effective reversible addition–fragmentation chain transfer (RAFT) agent for the RAFT polymerization of MMA. The polymerization showed “living”/controlled characteristics. Reaction kinetics was pseudo first order and linear. Relative molecular mass of polymer was controllable. The polymer obtained was narrow in polydispersity index (<1.5). However, in the cases of MTTCD and CPDB, they are not efficient enough to control the polymerization of MMA. The obtained polymers have broad molecular weight distributions. The derived well-controlled block copolymer PMMA-b-PDMAEMA and PMMA-b-PDMAEA were successfully prepared by using the above obtained polymer as macromolecular RAFT agent and DMAEMA or DMAEA as the second monomer. The molecular weight distributions are relatively narrow (most of $M_w/M_n < 1.3$). The PMMA-b-PDMAEA/PS composite membranes were prepared. The CO_2 and N_2 permeation performance were tested at different pressure. The results showed that the resulted composited membrane had a CO_2 permeation rate of 3.68×10^{-5} cm^3 (STP) $cm^{-2}s^{-1}cmHg^{-1}$ and a N_2 permeation rate of 1.78×10^{-7} cm^3 (STP) $cm^{-2}s^{-1}cmHg^{-1}$ and an ideal CO_2/ N_2 selectivity of 206.6 at a feed gas pressure of 7.6 cmHg and 30 ^oC.

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ABBREVIATIONS

MMA = methyl methacrylate

RAFT = Reversible addition fragmentation chain transfer

CTA = Chain transfer agent

AIBN = 2, 2´-Azo-bis(isobutyronitrile)

MTTCD = S-1-Dodecyl-S′-(α, α′-dimethyl-α-acetic acid) trithiocarbonate

BDATC = S,S′-bis (2-hydroxyethyl-2′-dimethylacrylate) trithiocarbonate

CPDB = 2-cyanoprop-2-yl dithiobenzoate

DMAEA = N, N-dimethylaminoethy acrylate

DMAEMA = N, N-dimethylaminoethyl methacrylate

OZ = 2-ethyl-2-oxazoline

TETA = trimethylene tetramine

TMC = hexane-soluble trimesoyl chloride

PES = polyethersulfone

PVP = polyvinylpyrrolidone

VSA-SA = N-vinyl-γ-sodium aminobutyrate-sodium acrylate copolymer

PVA = poly(vinyl alcohol)

PAA = Poly(acrylic acid)

AIBN = 2, 2´-Azo-bis(isobutyronitrile)

FTIR = Fourier Transform infrared spectroscopy

^{1}HNMR = ^{1}Nuclear Magnetic Resonance Spectroscopy

GPC = Gel Permeation chromatography

DSC = Differential Scanning Calorimetry

XRD = X-ray diffraction

SEC = Size exclusion chromatograph

PDI = polydispersity indice

M_n = Number-average molecular weight

M_w = Weight-average molecular weight

M/R/I = Monomer/RAFT agent/ Initiator

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