Chinese Journal of
POLYMER SCIENCE

RESEARCH ARTICLE

https://doi.org/10.1007/s10118-024-3085-9
Chinese J. Polym. Sci. **2024**, *42*, 711–717

Organic Brønsted Acid-Catalyzed Stereoselective Cationic RAFT Polymerization: The Effect of RAFT Agents

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Electronic Supplementary Information

Abstract The tacticity of vinyl polymers is a key factor affecting the properties of materials. Recently, organic Brønsted acids have been demonstrated as effective catalysts for the development of highly stereoselective cationic reversible addition-fragmentation chain transfer (RAFT) polymerizations of vinyl ethers, in which the use of RAFT agents could allow the control the molecular weight and tacticity of polymer products simultaneously. However, the effect of RAFT agents on the tacticity-regulation remains elusive and lacks of investigation. In this study, we synthesized four types of RAFT agents and evaluated their influence in the stereoselective cationic polymerization of isobutyl vinyl ether in the presence of PADI as a Brønsted acid catalyst, which unveils that the Z group of RAFT agents could not only affect the polydispersity of the products, but also exert a profound effect on the stereoselectivity. After extensive screening of the RAFT agents, high stereoregularity (isotacticity, 90% *m*) was obtained when using dithiocarbonate ester-type RAFT agents with a benzyloxy Z group.

Keywords Brønsted acid catalysis; Stereoselective cationic polymerization; RAFT polymerization; Chain transfer agents; Tacticity

Citation: Zhang, Z. Y.; Yang, Z.; Liao, Y.; Liao, S. H. Organic Brønsted acid-catalyzed stereoselective cationic RAFT polymerization: the effect of RAFT agents. *Chinese J. Polym. Sci.* **2024**, *42*, 711–717.

INTRODUCTION

Tacticity has a profound effect on the physical, thermal, and mechanical properties of vinyl polymers. Therefore, to achieve a high degree of control on this factor, considerable efforts have been dedicated to the catalyst development aiming to improve the stereoselectivity of polymerizations.[1–4] Poly(vinyl ether)s (poly(VE)s) also show significant tacticity-dependent properties.[5,6] For example, poly(isobutyl vinyl ether) (poly(IBVE)) with high isotacticity could exhibit the properties of a semi-crystalline thermoplastic with a high melting point (90% *m*, T_m>120 °C), while the atactic products is typically a fluid at room temperature. However, it is challenging to achieve a high stereoregulation in cationic polymerizations, due to the planar sp^2-configuration of the active carbocationic centre and the low reaction barrier (Fig. 1a-i).[7] Typically, harsh conditions like low temperature and high catalyst loadings are required to achieve a satisfactory isotacticity-regulation, and prevalently employed transition metal-based Lewis acid catalysts (*e.g.*, Ti complexes).[6–22] In the context of developing organic catalysts[23–27] for cationic polymerization to access metal-free polymers, we found that organic Brønsted acids could also deliver an excellent stereochemical control in the cationic polymerization of vinyl ethers. By employing bulky chiral acid like (IDPi)[23] and (PADI),[25] which are supposed to participate in the creation of a sterically confined asymmetric micro-environment around the active chain end *via* ion-pair interaction between the bulky anion of the acid catalysts and the active cationic centre (Fig. 1b), high isotacticity (upto 92% *m*) can be achieved at a low catalyst loading.

By integrating a reversible addition-fragmentation chain transfer (RAFT) process, the corresponding cationic RAFT polymerization showed high advantages in the synthesis of functional polymers with controlled molecular weights and well-defined polymer architectures (Fig. 1a-ii).[28–32] For example, in 2014, Kamigaito *et al.* reported an efficient cationic RAFT polymerization of vinyl ethers by using a ppm concentration of TfOH as catalyst. Particularly, the cationic RAFT polymerization products can be used in the synthesis of block copolymers *via* chain expansion by switching to a radical RAFT process.[28] However, this cationic RAFT polymerization is rarely achieved with a concurrent tacticity-regulation.[21,26,33] Recently, we found that in the cationic polymerization of vinyl ethers using PADI as an organic Brønsted acid catalyst/initiator in the presence of trithiocarbonates as a chain-transfer agent, a highly stereoselective cationic RAFT polymerization can be successfully established.[27] Notably, by virtue of the RAFT process, isotac-

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Received November 25, 2023; Accepted December 21, 2023; Published online January 25, 2024

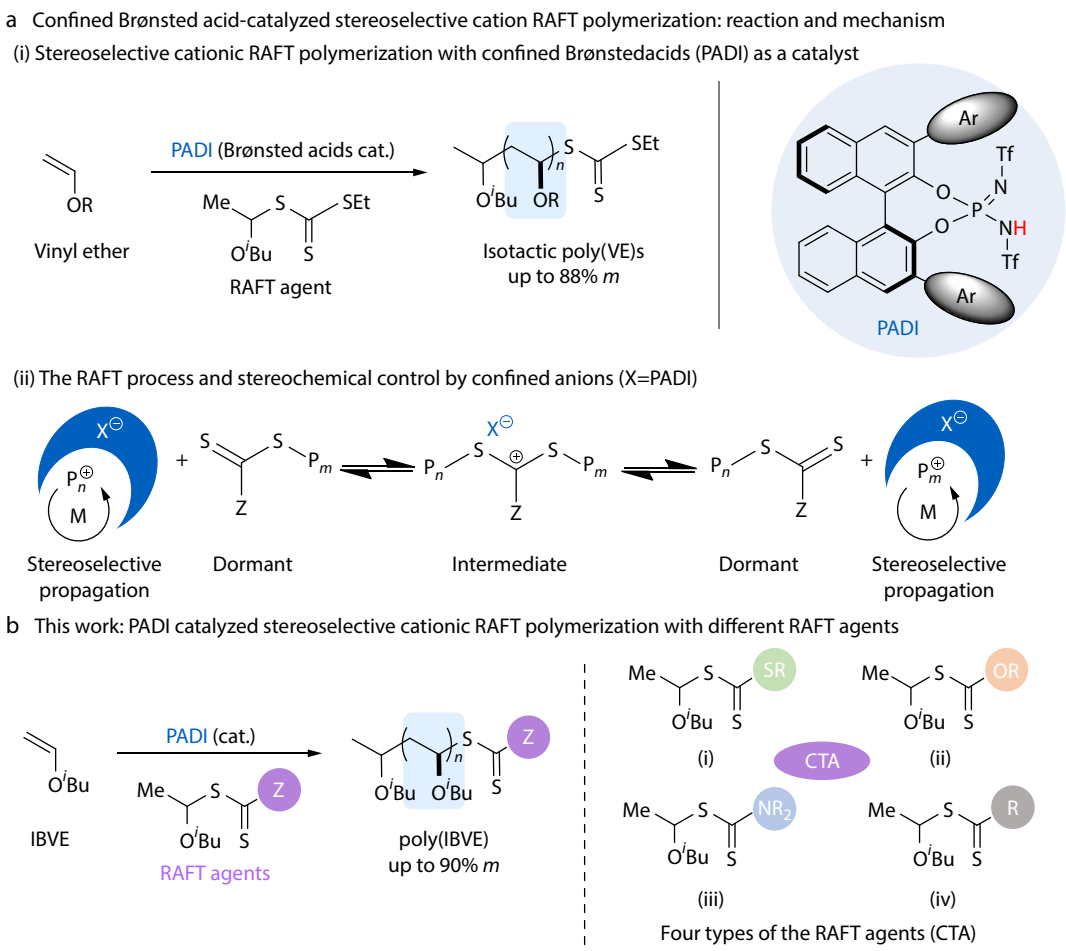


Fig. 1 (a) Confined Brønsted acid-catalysed cationic RAFT polymerization of vinyl ethers; (b) PADI-catalysed stereoselective cation RAFT polymerization with different RAFT agents.

tic poly(VE)s with high stereoselectivity, controlled molecular weight, and low dispersion became accessible at a low catalyst loading (down to 200 ppm). It is well-know that the RAFT agents play important roles in control over the molecular weight and polydispersity. However, it is still unclear how the structures of RAFT agents affect the stereochemistry of the cationic polymerization. Herein, we wish to report our study on this effect in the Brønsted acid-catalyzed stereoselective cationic polymerization. We synthesized and tested a series of RAFT agents ($CH_3CH(O^iBu)-S-C(Z)=S$, Z=SR; OR; NR_2; R), which unveils that the Z group could not only affect the molecular weight distribution of polymer products, but also influence the tacticity of the (poly(IBVE), even though the acid catalysts should play the pivotal role in the stereochemical control. After further optimization of the structure of RAFT agents, high stereoregularity (isotacticity, upto 90% *m*) was successfully obtained when using dithiocarbonate ester-type RAFT agents with a benzyloxy Z group.

EXPERIMENTAL

Materials

Isobutyl vinyl ether (IBVE) (99%,TCI) was dried over calcium hydride (CaH_2) (98%, J&K) for 12 h, collected under reduced pressure and stored in the glove box under an argon atmosphere at −20 °C. Toluene (AR) and hexane (AR) were distilled over Na for 24 h under an argon atmosphere and deoxygenized by freeze-pump-thaw cycle three times and stored in Schlenk flasks with 4 Å molecular sieves under argon atmosphere. PADI were prepared according to the literature procedure.[25] RAFT agents were synthesized according to literature procedures.[34,35] All other chemicals were purchased from Adamas-beta, Energy Chemical and Shanghai Chemical Reagents Co., Ltd., and used without further purification unless mentioned.

Characterization

^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR were recorded on Bruker AVIII 400 MHz or JEOL JNM-ECZ500R/S1 500 MHz in $CDCl_3$ with tetramethylsilane as the internal standard. The number-average molecular weight (M_n, GPC) and molecular weight distributions ($Đ$) of the obtained polymers were determined by a Waters 1515 series gel permeation chromatograph (GPC) equipped with a Waters 2414 refractive-index detector, using a Styragel HR3THF (7.8 × 300 mm) Column and a Styragel HR4THF (7.8 × 300 mm) Column with measurable molecular weights ranging from 10^2 g·mol^{-1} to 10^6 g·mol^{-1}. THF was used as eluent at a flow rate of 1.0 mL·min^{-1} at 40 °C. GPC samples were injected manually and Shodex Polystyrene samples of known molecular weight were used as calibration standards for the experimental number-average molecular weight (M_n) and molecular weight distribu-

tions (*Đ*). The degree of isotacticity was calculated by the ^{13}C-NMR backbone methylene resonances.[16]

Typical Procedure for Cationic RAFT Polymerization of IBVE with a PADI Catalyst and RAFT Agents

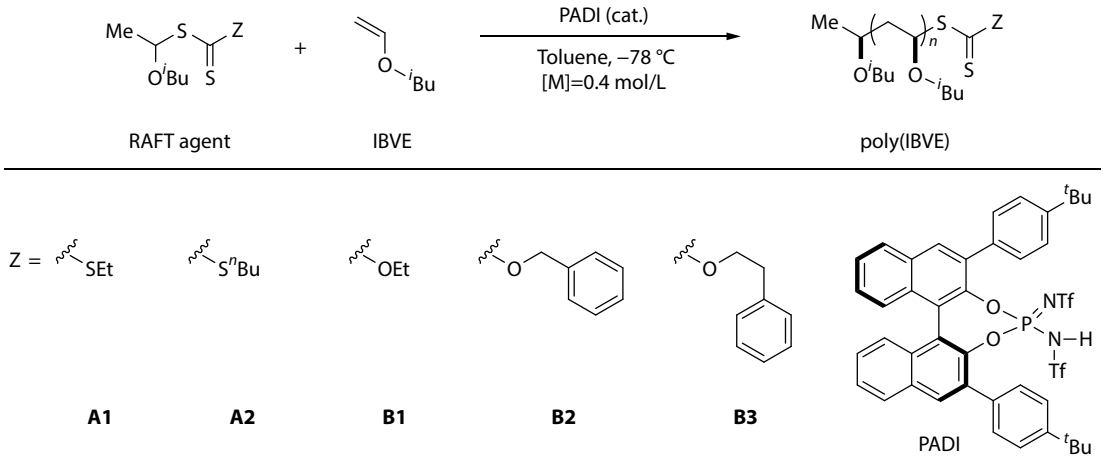
In an argon filled glovebox, isobutyl vinyl ether (IBVE, 200 mg, 2 mmol, 1 equiv.), RAFT agents (0.02 mmol, 0.01 equiv.), and dried solvent (4.0 mL) were added into a flame-dried Schlenk tube. At the same time, PADI (0.0005 equiv.) was added into another dried Schlenk tube and toluene (1.0 mL) was added to dissolve the catalyst. The Schlenk tube contained monomer solution was put in liquid nitrogen until all the solution freezed, and then the catalyst solution was added by syringe under positive argon atmosphere rapidly. Subsequently, the reaction mixture was put into a low-temperature reactor with ethanol as coolant and stirred at −78 °C for 30 min. Later on, the reaction was quenched by the addition of Amberlyst 21 and the reaction mixture stirred at room temperature for another 0.5 h. The Amberlyst 21 solid was removed by filtering and the solvent evaporated under reduced pressure to afford the crude poly(IBVE)s. The crude polymer was dissolved with THF (2 mL) and precipitated in MeOH (30 mL), affording the desired poly(IBVE)s as white solids (176 mg, yield 88%), and the polymer was analyzed by GPC and NMR.

RESULTS AND DISCUSSION

We initiated the study by investigating the stereoselective cationic polymerization of IBVE with PADI as the catalyst in the presence of different RAFT agents. The polymerizations were carried out at $[IBVE]_0$:$[RAFT\ agent]_0$:$[PADI]_0$ ratio of 100/1/0.05 in toluene at −78 °C. We first examined the di- and tri-thio carbonate ester-type of RAFT agents (Table 1). RAFT agent **A1** could afford poly(IBVE) with target molecular weight and high isotacticity (88% *m*, entry 1), which is consistent with our previous result.[25] Then, we tried RAFT agent **B1** with a lower C_{tr} than RAFT agent **A1**, and a slightly lower isotacticity was obtained (88% *m* versus 85% *m*, entry 1 versus 3). Later on, we modified the RAFT agent **A1** by substituting ethyl for *n*-butyl, but **A2** gave a similar stereoselectivity (entries 1 and 2 in Table 1). Nevertheless, in the course of optimization of dithio-carbonate ester-type RAFT agents (**B1**–**B3**), we found that the use of benzyl-substituted RAFT agents (**B2**, Z = OBn) could deliver a slightly higher isotacticity (entry 4, 89% *m*) than the tri-thio-carbonate-type agents (**A1** and **A2**).

Next, we examined the dithiocarboxylic ester-type RAFT agents (**C1**–**C3**) in the stereoselective cationic polymerization of IBVE under the same conditions (Table 2). Interestingly, we found an improvement in the stereoselectivity in the order of **C1**, **C2**, **C3**, affording 80% *m*, 85% *m*, and 86% *m*, respectively (entries 1–3 in Table 2), with a significant improvement by switching Z group from methyl to phenyl (entry 1 versus 2 in Table 2). Moreover, we further tested the carbamodithioate-type RAFT agents (entries 4 and 5 in Table 2). The RAFT agent **D1** afforded a much lower stereoselectivity, when comparing with the other three types (A, B and C) of RAFT agents, which is in line with our previous observation. Of note, **D1** could afford polymer product with a much narrower molecular weight distribution. Interestingly, by replacing the diethylamine group (—NEt_2) in **D1** with diphenylamine (—NPh_2), the isotacticity can be increased to 85% *m*. In Fig. 2, we selectively listed the results with different RAFT agents, with Z groups in the order of dialkylanimo- (—NEt_2), alkyl (—Me), alkoxyl (-OEt), and alkylthio- (—SEt), in which we could see a trend of increase in isotacticity-regulation. Of note, the benzyloxyl one (**B3**) remains the best one in terms of isotacticity regulation. In addition, a similar trend was observed when applying these RAFT agents to the polymeriza-

Table 1 Stereoselective cationic polymerization of IBVE with tri- or di-thio carbonate-type RAFT agents. [a]

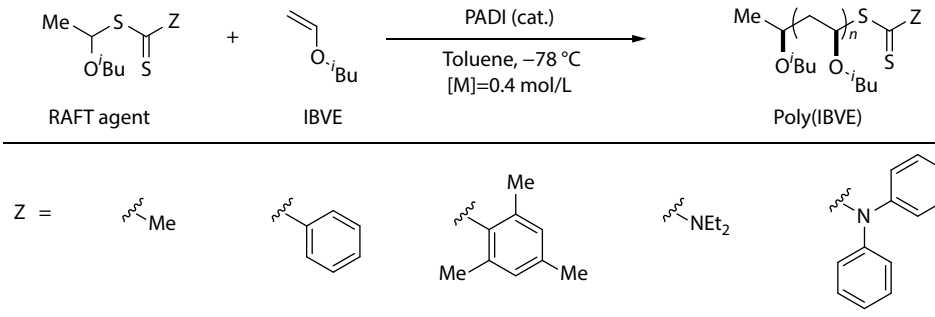


Entry	RAFT agent	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ [b] (g/mol)	$Đ$ [b]	*m* [c]
1	**A1**	10200	10700	1.35	88%
2	**A2**	10300	10000	1.73	88%
3	**B1**	10200	11000	1.56	85%
4	**B2**	10300	10700	1.65	89%
5	**B3**	10300	8500	1.60	85%

[a] $[IBVE]_0$:$[RAFT\ agent]_0$:$[PADI]_0$ ratio of 100:1:0.05 in toluene at −78 °C, 0.5 h; [b] M_n and $Đ$ were measured by GPC with polystyrene standards; [c] Determined by ^{13}C-NMR analysis.

https://doi.org/10.1007/s10118-024-3085-9

Table 2 Stereoselective cationic polymerization of IBVE with dithiocarboxylate-type and carbamodithioate-type RAFT agents. [a]



Entry	RAFT agent	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ [b] (g/mol)	$Đ$ [b]	m [c]
1	**C1**	10200	11000	1.93	80%
2	**C2**	10200	9300	1.80	85%
3	**C3**	10300	9000	1.73	86%
4	**D1**	10300	10200	1.20	75%
5	**D2**	10400	9000	1.48	85%

[a] $[IBVE]_0$:$[RAFT\ agent]_0$:$[PADI]_0$ ratio of 100:1:0.05 in toluene at −78 °C, 0.5 h; [b] M_n and $Đ$ were measured by GPC with polystyrene standards; [c] Determined by ^{13}C-NMR analysis.

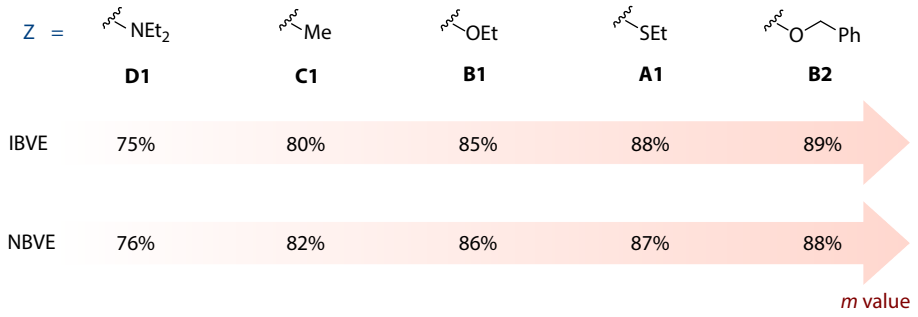


Fig. 2 Polymer tacticity corresponding to different RAFT agents.

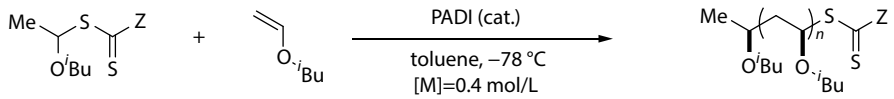
tion of *n*-butyl vinyl ether (NBVE).

Further, considering the possible tuning electronic nature of the phenyl group in **C2** and **D2**, we synthesized RAFT agent **C4**, **C5**, **C6**, as well as **D3**, **D4** and **D5** (Table 3). For comparison, these new RAFT agents were tested under the same conditions in the polymerization of IBVE at $[IBVE]_0$:$[RAFT\ agent]_0$:$[PADI]_0$ ratio of 100/1/0.05 in toluene at −78 °C. As shown in Table 3, the electronic tuning unveiled no significant difference in terms of stereoselectivity, while the electron-rich one (**C4**) afforded a better control in terms of low dispersity ($Đ$ 1.58 versus 1.80, 1.92, entry 2 versus entries 1 and 3 in Table 3). In cases of carbamodithioate-type RAFT agents (**D1**–**D5**), low dispersities ($Đ$=1.20–1.56) were observed in general. Regarding the tacticity-regulation, the four RAFT agents **D2**, **D3**, **D4** and **D5**, gave quite similar results (Table 3, entries 4–6). According to the RAFT process (Fig. 1a-ii), there is a shift of the bulky anion (X^- = $PADI^-$) from chain end P_n^+ to P_m^+. In principle, only the contact ion pair form (P_n^+/ $PADI^-$) could reach an effective stereochemical control by the bulky anion of PADI. The frequency and speed of this shift process should be affected by the RAFT agents, and the recombination of the ion pairs to generate a contact one would leave a time gap, in which less effective stereochemical control could happen. In other words, the loose ion pairs of P_n^+ or P_m^+/$PADI^-$ (before they become contact ion pairs) could also initiate monomer insertion but with lower stereoselectivity and lower isotacticity. Therefore, RAFT agents that could reduce the frequency of this anion shift process or speed up the re-generation of contact ion pairs should favour the stereochemical control. This could be a reason why RAFT agents with a lower chain-transfer constant and bulky Z groups could often afford a better stereoselectivity. The effect of RAFT agents on stereoselectivity remains complicated so far to elucidate, while these results and the comparison of different types of RAFT agents provide us a tentative guide for choosing a suitable one to develop an effective stereoselective cationic RAFT polymerization process.

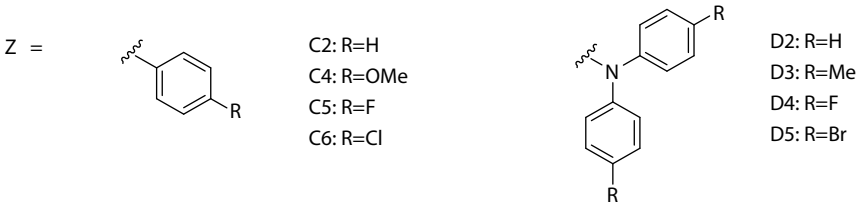
With RAFT agent **B2** providing the highest isotacticity among the RAFT agents examined, we further investigated the effect of solvent with PADI as the catalyst and **B2** as the RAFT agent (Table 4). A series of solvents were tested by mixing with toluene, and non-polar solvent like methylcyclohexane and *n*-hexane were found giving higher isotacticity, when compared with polar solvents like DCM and $CHCl_3$ (entries 1–4 in Table 4). We thus further screened the mixed solvent by adjusting the ratio of toluene with methylcyclohexane (entries 5–7 in Table 4) and *n*-hexane (entries 8–10 in Table 4), respectively. Pleasingly, the content of *meso* diads can be was further increased to 90%, by using toluene/methylcyclohexane 2/3 as a solvent (entry 6 in Table 4). Moreover, high stere-

https://doi.org/10.1007/s10118-024-3085-9

Table 3 Further electronic tuning on RAFT agent **C2** and **D2**. [a]



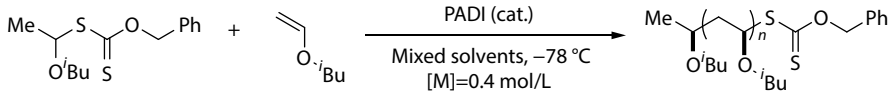
RAFT agent IBVE poly(IBVE)



Entry	RAFT agent	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ [b] (g/mol)	$Đ$ [b]	m [c]
1	**C2**	10200	9300	1.80	85%
2	**C4**	10300	8500	1.58	84%
3	**C5**	10300	10000	1.92	85%
4	**C6**	10300	13200	1.87	85%
5	**D2**	10300	9000	1.48	85%
6	**D3**	10400	9000	1.56	84%
7	**D4**	10400	9000	1.55	85%
8	**D5**	10500	9600	1.58	84%

[a] $[IBVE]_0$:$[RAFT\ agent]_0$:$[PADI]_0$ ratio of 100:1:0.05 in toluene at −78 °C, 0.5 h; [b] M_n and $Đ$ were measured by GPC with polystyrene standards; [c] Determined by ^{13}C-NMR analysis.

Table 4 Solvent effect in stereoselective cationic RAFT polymerization of IBVE with RAFT agent **B2**. [a]



RAFT agent: **B2** IBVE Poly(IBVE)

Entry	Solvent	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ [b] (g/mol)	$Đ$ [b]	m [c]
1	Tol/DCM 4/1	10300	8000	1.66	84%
2	Tol/$CHCl_3$ 4/1	10300	9000	1.59	83%
3	Tol/MeCy 4/1	10300	13600	1.76	86%
4	Tol/*n*-hexane 4/1	10300	11900	1.77	86%
5	Tol/MeCy 3/2	10300	14000	1.90	87%
6	Tol/MeCy 2/3	10300	15100	1.94	90%
7	Tol/MeCy 1/4	10300	16000	1.90	85%
8	Tol/*n*-hexane 3/2	10300	11000	1.71	90%
9	Tol/*n*-hexane 2/3	10300	13000	1.85	90%
10	Tol/*n*-hexane 1/4	10300	12000	1.76	88%

[a] $[IBVE]_0$:$[RAFT\ agent]_0$:$[PADI]_0$ ratio of 100:1:0.05 in toluene at −78 °C, 0.5 h; [b] M_n and $Đ$ were measured by GPC with polystyrene standards; [c] Determined by ^{13}C-NMR analysis. MeCy: methylcyclohexane.

oregularity (90% *m*) was successfully obtained by increasing the proportion of *n*-hexane (entries 8 and 9 in Table 4). To the best of our known, 90% *m* represents the highest isotacticity achieved so far in the stereoselective cationic RAFT polymerization of IBVE.

CONCLUSIONS

In summary, the effect of RAFT agents on tacticity was examined in the stereoselective cationic RAFT polymerization of isobutyl vinyl ether, by synthesizing and testing four types of RAFT reagents by varying the Z groups. It was found that, even though the stereoselectivity of the polymerization is mainly governed by the bulky chiral anion (PADI), the RAFT agents could also exert an important influence on the stereoselectivity. Pleasingly, through the optimization of the Z group, unprecedented high isotacticity (up to 90% *m*) was successfully achieved in this cationic RAFT polymerization by using dithiocarbonate ester-type RAFT agents in which Z is a benzyloxy group. We hope this study could serve as a preliminary guide in choosing a suitable RAFT agent for the development of stereoselective cationic RAFT polymerization with a given process or monomer.

Conflict of Interests

The authors declare no interest conflict.

https://doi.org/10.1007/s10118-024-3085-9

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-024-3085-9.

ACKNOWLEDGMENTS

This work was financially supported by the Recruitment Program of Global Experts of China, the National Natural Science Foundation of China (Nos. 21602028 and 22371240), Beijing National Laboratory for Molecular Sciences (No. BNLMS201913), 100-Talent program of Fujian, Fuzhou University and Xiamen University.

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https://doi.org/10.1007/s10118-024-3085-9