Effect of Molecular Weight on CO₂-philicity of Poly(vinyl acetate) with Different Molecular Chain Structure

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ABSTRACT

The low molecular weight, topological structure and end group removal are expected to enhance the CO₂-philicity of poly(vinyl acetate) (PVAc), which is of great interest for expanding CO₂ applications as a green solvent. This work aims at investigating the effect of molecular weight (M_n) of PVAc with different molecular chain structure on the CO₂-philicity through dissolution behavior measurement and molecular modeling. Well-defined 3-armed and 4-armed R-core PVAc was synthesized by RAFT polymerization, and then the corresponding xanthate groups were removed. The CO₂-philicity of multi-armed PVAc was found to be inferior to that of linear one at low M_n . With increasing the M_n from 1000 to 7000 g/mol, the cloud point pressures (P_c) of multi-armed PVAc first decreased, reached a minimum at a given M_n , and then increased, which was different from the variation trend of the P_c of linear PVAc versus M_n . In addition, removal of the xanthate groups could effectively enhance the CO₂-philicity of PVAc, especially at low M_n . Moreover, the molecular dynamics (MD) simulations on the interactions in polymer/CO₂ systems indicated that the multi-armed structure had different effects on the compatibility with CO₂ at different M_n . At low M_n , the polymer-polymer interaction was the main driving force deciding the CO₂-philicity due to the significant difference in different molecular chain structures. At high M_n , multi-armed structure enhanced the CO₂-philicity due to the synergistic effect of moderate polymer-polymer interaction and large polymer-CO₂ interaction. The appropriate molecular chain structure could be selected to enhance the CO₂-philicity of PVAc at a certain M_n .

KEYWORDS: Poly(vinyl acetate); CO₂-philicity; Molecular chain structure; Cloud point pressure; Molecular dynamics simulations

1. INTRODUCTION

With the improvement of people's environmental awareness, supercritical carbon dioxide (scCO₂) has intensively emerged as a potential alternative to the common employed conventional organic solvents for industrial applications [1, 2] due to its environmentally benign, non-flammability, low price and moderate critical temperature and pressure ($T_{\text{crit}} = 31.1\text{ }^{\circ}\text{C}$, $P_{\text{crit}} = 7.38\text{ MPa}$) [3-6]. Unfortunately, due to its weak polarity and low dielectric constant [11, 12], scCO₂ is a poor solvent toward macromolecules and polar biomolecules. Only fluoropolymers [7, 8] and silicone-based polymers [9, 10] exhibit relatively good CO₂-philicity. Notably, both of them have a common property of weak polymer-polymer interactions relating to low cohesive energy density [10, 13]. Besides, the CO₂-philic polymers have other features in common presenting as high entropy of mixing and strong cross-interactions with CO₂, which were proposed by Beckman et al [14].

Whereas, both of fluoropolymers and silicone-based polymers are expensive and non-biodegradable, causing them unfavorable to be widely applied. Efforts have been devoted to discover or synthesize green CO₂-philic polymers with low cost [15, 16]. In comparison to the other hydrocarbon polymers such as poly(propylene oxide) (PPO), polylactic acid (PLA) and poly(methyl acrylate) (PMA), PVAc has a relatively significant solubility in CO₂. PVAc with number-average molecular weight of 3090 g/mol can dissolve at 37.6 MPa and 25 °C with a loading of 5 wt% [17]. The main difference in the CO₂-philicity of these polymers is attributed to accessibility of the functional groups containing carbonyl moieties (such as electron-rich acetate groups) which will cause favorable interactions with the CO₂ solvent [17,

18]. The specific attractive interaction between CO₂ and carbonyl groups had been confirmed by Kazarian et al using the FT-IR spectroscopy [19]. Meanwhile, the ab initio calculations also indicated that C-H...O hydrogen bonds [20] and weak Lewis acid-Lewis base interactions [21] would enhance the stability of the binding between CO₂ and carbonyl groups. But even so, the solubility of PVAc in CO₂ was much lower than that of fluoropolymers due to the strong polymer-polymer interaction [22, 23].

To circumvent these intrinsic limitations, different kinds of comonomers have been chosen to synthesize PVAc-based copolymer with enhanced solubility in CO₂. Howdle et al. [24] demonstrated that poly(vinyl acetate-*alt*-dibutyl maleate) (PVAc-*alt*-PDBM) copolymers showed a significant increased solubility in CO₂ approaching that of perfluoropolyether (PFPE) and poly(dimethylsiloxane) monomethacrylate (PDMS-mMA). Molecular dynamics (MD) simulations by Hu et al. [25] also confirmed that PVAc-*alt*-PDBM had the relatively higher CO₂-philicity because of the weaker polymer-polymer interaction in comparison to other comonomers including dimethyl maleate (DMM) and diethyl maleate (DEM). Furthermore, introduction of monomer such as vinyl butyrate [26], vinyl pivalate (VPi) [27] and 1-(trifluoromethyl) vinyl acetate [28], could also reduce the P_c in comparison with the PVAc homopolymer. The topological structure [10, 14] and end-group treatment [14, 29] are also expected to weaken the polymer-polymer interaction, resulting in increasing their solubility in CO₂. Mohamed et al. [30] proposed that the existence of branched hydrocarbon tails would sufficiently reduce surface energy which was conducive to improve the CO₂ compatibility. Since that, the branch effect on solubility of CO₂-philes had attracted a lot of

research attentions. Tan et al. [33] synthesized a series of PVAc with different topologies using RAFT polymerization with Z-core xanthates, where the xanthate groups served as the core of the transfer agent. Their results showed that the PVAc with more arms had higher solubility in CO₂ at about 3500 g/mol. While, when continuing increasing the branching up to 1700 g/mol its solubility would decrease, which might be attributed to the deleterious effect of the carbonate linker (used to attach the end group) on the solubility of PVAc in CO₂ [34]. Besides, modification of the end groups with favorable functionalities could also significantly improve the polymer solubility in scCO₂. Gregorowicz et al. [35] demonstrated that end-capping hyperbranched polyethers and polyester with trifluoroacetic acid anhydride or trimethylchlorosilane could enhance their CO₂-philicity. Whereas, modification of the hydroxyl terminated PVAc with organic alcohols, such as phenylmethanol and hexanol, were not conducive to decrease the miscibility pressure [29]. Fedor et al. [36] also suggested that the solubility of polymer in supercritical fluids, especially at the low molecular weight, was significantly affected by the end groups. Thus, the low molecular weight, topological structure and xanthate group removal might be expected to enhance the CO₂-philicity of PVAc. Nevertheless, rare studies have been comprehensively carried out to focus on the combined effect of topological structure and molecular weight on branched CO₂-philes.

This work aims at investigating the effect of molecular weight of PVAc with different molecular chain structure on the CO₂-philicity through dissolution behavior measurement and molecular modeling. Multi-armed R-core PVAc was first synthesized by RAFT polymerization with well-defined M_n distributions, and then the corresponding end groups

were removed. The cloud point measurements of the samples were performed by using variable volume view cell. To obtain a deeper understanding on the interactions of polymer/CO₂ systems, MD simulations were introduced to access the effect of molecular weight and chain structure on the interaction energy, cohesive energy density (CED), and Flory-Huggins interaction parameter between CO₂ and different PVAc chain. In addition, the surface tensions were also measured to verify the variation trend of polymer-polymer interaction. Furthermore, the radial distribution functions (RDF) for polymer/CO₂ systems was applied to analyze the inter-molecular interactions at the molecular level. On the basis of the experimental and molecular modeling results, the effect of molecular weight on CO₂-philicity of PVAc with different molecular chain structure was explored.

2. EXPERIMENTAL SECTION

2.1. Materials

Vinyl acetate (VAc, 99.0%, Aladdin) was purified to remove the inhibitor by washing with saturated sodium bisulfite three times, distilled water once, and sodium carbonate aqueous solution (10 wt%) twice, respectively. Thereafter, it was washed to neutral and dried by magnesium sulfate anhydrous. 2',2'-Azobis (isobutyronitrile) (AIBN, 97%, Aladdin) was recrystallized twice from ethanol and vacuum-dried before used, and lauroyl peroxide (LPO, 98%, Aladdin) was also recrystallized from toluene. Other reagents were all purchased from Aladdin Chemical Co., Ltd., and used without further purification.

2.2. Synthesis of Multifunctional Xanthate Agent

R-core 3-armed xanthate agent (RAFT-3). A solution of 1,1,1-Tris(hydroxymethyl) ethane (2.40 g, 0.02 mol), pyridine (5.0 mL) and anhydrous chloroform (30.0 mL) was added into a 100 mL round-bottom flask. The flask was then placed in an ice-water bath. After adding 2-bromopropionyl bromide (14.86 g, 0.07 mol) dropwise within 30 min, the bath was removed and the solution was kept magnetic stirring at room temperature for 60 hours. Diluted hydrochloric acid (50 mL, 10 v%) was then added into the solution. The organic phase was washed using aqueous sodium hydrogen carbonate (100 mL, 5 wt%) and dried with magnesium sulfate anhydrous. After the solvent was distilled under reduced pressure, the bromide intermediate product was obtained. Thereafter, a solution of the bromide intermediate product (6.48 g, 0.01 mol), potassium ethyl xanthogenate (8.0 g, 0.05 mol) and chloroform (100 mL) was added into a 250 mL flask and kept magnetic stirring for 3 days. The excessive potassium ethyl xanthogenate was then filtrated and washed several times with chloroform. The final RAFT-3 was obtained after distillation. ¹HNMR (CDCl₃): 0.97 (t, 3H, CH₃-C), 1.35 (m, 9H, CH₃-CH₂-O), 1.52 (b, 9H, CH₃-CH-S), 3.98 (q, 6H, C-CH₂-O), 4.34 (r, 3H, CH-S), 4.57 (s, 6H, CH₃-CH₂-O). ¹³CNMR (CDCl₃): 14.30 (CH₃-CH₂-O), 17.49 (CH₃-CH-S), 39.48 (C-C-C), 47.73 (CH-S), 67.20 (C-CH₂-O), 71.13 (CH₃-CH₂-O), 171.52 (C=O), 212.61 (C=S).

R-core 4-armed xanthate agent (RAFT-4). The synthetic method of RAFT-4 was similar to that of RAFT-3 and the biggest difference was the raw materials (as shown in Scheme 1). The bromide intermediate of RAFT-4 was synthesized with pentaerythritol and 2-bromopropionyl bromide as raw materials. A solution of pentaerythritol (2.70 g, 0.02 mol), pyridine (5.0 mL) and anhydrous chloroform (30.0 mL) was added into a 100 mL

round-bottom flask and then placed into an ice-water bath. After adding 2-bromopropionyl bromide (19.10 g, 0.09 mol) dropwise within 30 min, the bath was removed and the solution was kept magnetic stirring at room temperature for 60 hours. The after-processing was same as that of RAFT-3. Thereafter, a solution of the bromide intermediate product (8.40 g, 0.01 mol), potassium ethyl xanthogenate (10.1 g, 0.60 mol) and chloroform (100 mL) was added into a 250 mL flask and kept magnetic stirring for 3 days. The final product (RAFT-4) was obtained after removing the solvent. ^1H NMR (CDCl_3): 1.42 (t, 12H, $\text{CH}_3\text{-CH}_2\text{-O}$), 1.58 (m, 12H, $\text{CH}_3\text{-CH-S}$), 4.14 (b, 8H, $\text{C-CH}_2\text{-O}$), 4.41 (q, 4H, CH-S), 4.63 (r, 8H, $\text{CH}_3\text{-CH}_2\text{-O}$). ^{13}C NMR (CDCl_3): 14.19 ($\text{CH}_3\text{-CH}_2\text{-O}$), 17.24 ($\text{CH}_3\text{-CH-S}$), 43.05 (C-C-C), 47.69 (CH-S), 63.50 ($\text{C-CH}_2\text{-O}$), 71.30 ($\text{CH}_3\text{-CH}_2\text{-O}$), 171.45 (C=O), 212.49 (C=S).

2.3. RAFT Solution Polymerization of Multi-armed PVAc

A solution of AIBN (0.36 g, 2.22 mmol), 3-armed R-core star xanthate agent (2.87 g, 4.44 mmol), VAc (9.46 g, 0.11 mol) and THF (6.0 mL) was added into a 100 mL round-bottom flask, which was connected to the condenser-west tube and sealed. The solution was degassed using several argon-vacuum cycles, and then placed in a constant temperature water-bath at 60 °C with magnetic stirring for several hours. The reaction products were dissolved into THF and then precipitated in cold hexane. After vacuum drying at 35 °C for 48 h, the products were obtained and measured by GPC and NMR. The 4-armed R-core PVAc was also synthesized following the same procedure.

2.4. Removal of Xanthate Groups from multi-armed PVAc

A solution of PVAc (3.87 g, $M_{n, GPC} = 8417$ g/mol, 0.46 mmol), 2-propanol (8 mL), LPO (0.6 g, 1.5 mmol) and THF (8 mL) was first prepared in a 100 mL round bottom flask and sealed. The solution was degassed using several argon-vacuum cycles, then placed into oil-bath with 80 °C constant temperature and kept magnetic stirring for 6 hours. The samples were dissolved into THF, and precipitated in cold hexane. The final products were obtained after vacuum drying for 48 h at 35 °C and characterized by GPC and NMR.

2.5. Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV spectrometer (400 MHz) with $CDCl_3$ as the solvent at ambient temperature, where tetramethylsilane (TMS) was used as an internal reference. Gel permeation chromatography (GPC, Agilent 1100) was performed using refractive index detector (RID) and a chromatography column (PL gel 5 μ m). THF was used as an eluent at a flow rate of 1.0 mL/min with monodispersed polystyrene as a calibration standard.

The water contact angle measurements were examined by using a sessile drop tensiometer (Datephysics, model OCA20, Germany) at room temperature. An accurate amount of polymer was dissolved in 2-butanone and filtered through a 0.45 μ m Nylon filter to obtain a polymer solution of 10 wt%. Then, the dried homogeneous polymer film was prepared by spin-coating on a clean glass slide at a constant spinning rate of 1500 rpm for 60 s. The water drop (2 μ L) was deposited on the surface of the coated slide and analyzed by

drop shape analysis software. Each measurement was repeated for five times and averaged.

2.6. Solubility measurements in *scCO*₂

A high-pressure variable volume view cell (from 25.0 to 50.0 mL) which had been described previously [25] was used to measure the P_c of the polymers in *scCO*₂. In a typical experiment, an accurate amount of polymer (0.2 wt% based on the weight of injected *CO*₂) was placed at the bottom platform of the cell. The sealed cell was heated to 35 °C with a slow flow of *CO*₂ to remove the air in 5 minutes. Then, the pressure of the system increased by injecting pure *CO*₂ with a booster pump. With increasing pressure and stirring, the polymer completely dissolved in *CO*₂. After the system stabilized, the cell volume was enlarged slowly to reduce the pressure. The single transparent homogeneous phase would become cloudy at a certain pressure, that was, the cloud point pressure (P_c). All the P_c of the samples in *CO*₂ were repeated 3 times and the deviation of the P_c was usually no more than ± 0.1 MPa.

3. COMPUTATION SECTION

In the dissolution process of polymer in *CO*₂, polymer-*CO*₂ interaction and polymer-polymer interaction are the important parameters for screening suitable *CO*₂-philic polymers. They should be considered simultaneously to predict the compatibility between polymer and *CO*₂. MD simulations were implemented to evaluate the inter-molecular interaction and cohesive energy density (CED) in the polymer/*CO*₂ systems by using Material Studio software package in this work. The condensed-phase optimized molecular potential for atomistic simulation studies force field (COMPASS) [37] was applied to describe the

potential energy functions of all atoms in the simulations. COMPASS, an all-atom force field on the basis of the *ab initio* calculations and the optimization with experimental data, has been validated to be capable of predicting the structural and thermo-physical properties of hydrocarbon polymers [37, 38] and CO₂ [39]. The force field parameters of COMPASS used in this study had been listed in our previous work [25, 37-42] according to Sun et al. work [37-42].

The PVAc chains with different repeat units were constructed corresponding to different M_n from 2580 to 6450 g/mol. Meanwhile, the PVAc chains with 3-armed and 4-armed structure were built by using substantially the same molecular weight of the PVAc chains (Each arm had approximately the same number of repeating units in a multi-armed PVAc). Three kinds of simulation boxes were built with periodic boundary condition in Amorphous Cell approach, namely, the pure polymer system (linear, 3-armed and 4-armed structure with different M_n , and the number of repeat units are about the same in each box), the polymer/CO₂ system introducing 1000 CO₂ molecules based on the pure polymer system, and the polymer/CO₂ system containing 1000 CO₂ molecules and one polymer chain. The simulation boxes with different compositions of PVAc and CO₂ are gathered in Table 1. The subscript of PVAc₃₀ refers to PVAc with 30 repeat units, and the abbreviation of PVAc₃₀₋₃ represents the PVAc with 3-armed structure and a total of 30 repeat units. Wherein, the simulation cases involving linear PVAc₅₀ had been simulated in our previous work [43].

The optimized calculation box was annealed from 300 to 500 K for five circles after the

minimization of energy. Then the calculation was performed in the NVT ensemble for 100 ps with the time step of 1 fs at 35 °C, and subsequent NPT ensemble for 300 ps at 35 °C, 20 MPa. In all the calculations, the system temperatures and the pressures of NPT ensemble were kept by using the Andersen method. The vdW interactions were evaluated by using the atom-based summation while the electrostatic interactions were calculated by using the Ewald summation. The configurations of final 50 ps were collected to analyze the thermodynamic parameters containing CED and system energy. The detailed calculation procedures can be found in our previous work [25].

Table 1. Systems with different compositions of PVAc and CO₂ in MD simulations

System	Composition	M_n of a chain	Number of chains	Number of units in a chain	Number of CO ₂
1	PVAc ₃₀	2582	10	30	-
2	PVAc ₃₈	3270	8	38	-
3	PVAc ₅₀	4302	6	50	-
4	PVAc ₆₀	5162	5	60	-
5	PVAc ₇₅	6452	4	75	-
6	PVAc ₃₀ -CO ₂	2582	1	30	1000
7	PVAc ₃₈ -CO ₂	3270	1	38	1000
8	PVAc ₅₀ -CO ₂	4302	1	50	1000
9	PVAc ₆₀ -CO ₂	5162	1	60	1000
10	PVAc ₇₅ -CO ₂	6452	1	75	1000
11	PVAc ₃₀ -CO ₂	2582	10	30	1000
12	PVAc ₃₈ -CO ₂	3270	8	38	1000
13	PVAc ₅₀ -CO ₂	4302	6	50	1000
14	PVAc ₆₀ -CO ₂	5162	5	60	1000
15	PVAc ₇₅ -CO ₂	6452	4	75	1000

4. RESULTS AND DISCUSSION

4.1. Controlled/living Solution Polymerization of R-core Multi-armed PVAc with R-core Multifunctional Xanthate Agents

By using the core-first strategy of the RAFT polymerization with the Z-core star xanthate agent, it is unable to remove the thiocarbonylthio groups of star PVAc because they serve as the linkage in the core while the star polymer arms grow [33, 44]. While another xanthate agent (the R-core xanthate agent) has a special structure that the reactive RAFT groups (the thiocarbonylthio groups) are in the end of the star structure. Thus, the thiocarbonylthio groups remain in the end while the star arms grow, providing convenience to remove the xanthate end group. In addition, the molecular weight as well as molecular structure can be well controlled by the R-core multifunctional star xanthate agent [45].

In this work, the 3-armed and 4-armed R-core star xanthate agent were synthesized as shown in Scheme 1 and then used as the chain transfer agent for the RAFT polymerization of the multi-armed PVAc, which was performed at 60 °C with AIBN as the initiator and THF as the solvent. In the case of ¹HNMR analysis for 4-armed PVAc, the chemical shift of the H atom belonging to RAFT-4 in b, e, a (as shown in the Figure 1a) are observed at 4.63 ppm, 4.14 ppm, 1.42 ppm, respectively. The area integration ratio of these peaks agrees well with the theoretical value (2:2:3). Figure 1b is the ¹HNMR spectrum of 4-armed PVAc polymerized by RAFT-4. The chemical shift of b, e, a remain the same, while the proton of i shifts from 4.41 to 2.21. The methane, methylene and methyl protons in the main chain of the 4-armed

PVAc with the thiocarbonylthio end groups show broad complex peaks (d, c and f) at 4.75-5.10 ppm, 1.55-1.95 ppm and 1.95-2.20 ppm, respectively, resulting from stereoisomers. The area ratio of the peaks d, c and f is 43:100:140, which is approximately 1:2:3 and consistent with the expected value. These results demonstrate that the 4-armed R-core star PVAc has been successfully synthesized. The ^1H NMR analysis for 3-armed PVAc was shown in Figure S1 of the Supporting Information.

Scheme 1. Synthesis route of multi-armed PVAc with end treatment.

Figure 1. ^1H NMR spectra of (a) 4-armed R-core star xanthate agent and corresponding (b) 4-armed R-core star PVAc and (c) the end-removed product.

Figure 2. Evolution of the molecular weight and dispersity of molecular weight distribution with conversion for polymerization with two 3-armed and 4-armed RAFT agents of VAc at 60 °C. The lines only indicate the trend.

Figure 2 shows the dependences of the M_n and the dispersity of molecular weight distribution ($\bar{D}$) on the conversion for the polymerization of the star PVAc with 3-armed and 4-armed R-core star xanthate agents, respectively. Both of these two systems had a narrow

molecular weight distribution (as illustrated in Figure S2 in the Supporting Information). The approximately linear dependence of the molecular weight on the conversion reveals that the conversion increases with increasing molecular weight, confirming that the RAFT solution polymerizations of PVAc performs in the presence of the 3-armed and 4-armed R-core star xanthate agents are generally completed with good controlled/living. As a result, the target R-core star PVAc with the low molecular weight and narrow molecular weight distribution could be well controlled by transforming the ratio of VAc monomer and chain transfer agent or changing the reaction time. Convinced by these results, plenty of multi-branched polymers with different target molecular weight and narrow molecular weight distribution were successfully synthesized as shown in Table 2. The GPC traces for the samples are exhibited in Figure S3 of the Supporting Information.

Figure 3. Gel permeation chromatograms for two samples of (a) 3-armed PVAc and (b) 4-armed PVAc and the products obtained by their reduction with dilauroylperoxide in 2-propanol (80 °C/6 h). Peak molecular weights are exhibited on the chromatograms.

Table 2. Experiment result for the synthesis of linear and multi-armed PVAc

entry	sample	$M_{n,theo}$ (g/mol) ^b	$M_{n,GPC}$ (g/mol) ($\bar{D}$) ^c	DP ^d	$M_{n,NMR}$ (g/mol) ^d	end group removal(%) ^d
1	PVAc-X ^a	1700	1881 (1.17)	18	1700	97.4
2	PVAc-X	3400	4113 (1.27)	42	3700	96.0
3	PVAc-X	5200	5563 (1.58)	66	5800	97.1
4	PVAc3-X	2200	1282 (1.29)	12	1636	98.2
5	PVAc3-X	3600	2482 (1.32)	32	3394	99.0
6	PVAc3-X	2700	2947 (1.17)	21	2374	98.7
7	PVAc3-X	4400	4419 (1.15)	41	4099	96.2
8	PVAc3-X	7400	8417 (1.21)	78	7200	97.1
9	PVAc4-X	2400	1534 (1.24)	15	2090	97.2
10	PVAc4-X	2900	2088 (1.23)	25	2898	96.4
11	PVAc4-X	4400	3465 (1.28)	41	4255	97.2
12	PVAc4-X	5500	4303 (1.36)	53	5249	96.9
13	PVAc4-X	7200	5959 (1.34)	77	7285	96.7

^aPVAc: linear PVAc, PVAc3: 3-armed PVAc, PVAc4: 4-armed PVAc, X: thiocarbonylthio end-group.

^b $M_{n,theoretical}=[VAc]_0 \times M_w(VAc)/[RAFT]_0 \times \text{conv}(VAc) + M_w(RAFT)$. ^cDetermined by GPC in THF with

PS standards. ^dCalculated by ¹HNMR in CDCl₃: $DP=N_{arm} \times (1 + d: (\frac{b}{2}))$, $M_{n,NMR}=DP \times M_w(VAc) +$

M_{RAFT} , Efficiency of end group removal $\eta = \left(1 - (\frac{d}{f})_{after}/(\frac{d}{f})_{before}\right) \times 100\%$. The molecular weight of end-removed samples were calculated by the following formula: $M_{n,rem}=M_{n,NMR} \times [1 - M(\text{end group}) \times \eta]$. The linear PVAc was synthesized by RAFT polymerization with a commercial RAFT agent (*O*-ethyl-*S*-(1-methoxycarbonyl) ethyl dithiocarbonate) and the corresponding thiocarbonylthio end-group was also removed.

Previous researchs [24, 46] indicated that CO₂-philicity of RAFT synthesized polymer could be negatively affected by the thiocarbonylthio group, especially for those with low molecular weight. Moreover, the star structure of the polymer was considered to multiply the end-group effect. We chose dilauroylperoxide (LPO) as the initiator, and 2-propanol as the H

atom donor to remove thiocarbonylthio end-groups which had been successfully used by Tong [47]. All the thiocarbonylthio groups could be got rid of after six hours of radical-induced reduction as demonstrated in Figure 1c. Comparing with the former polymer in Figure 1b, the peaks of *a* and *b* on the thiocarbonylthio end groups were clearly disappeared and their influence on the adjacent H atom reduced. In addition, the signals of protons from the other functional groups remained. GPC analysis shown in Figure 3 also indicated that there was no significant change in the molecular weight distribution and an expected small drop in the molecular weight associated with end group loss was observed.

4.2. Cloud Point Pressures of PVAc with different molecular structure in scCO₂.

In the high-pressure variable volume view cell, the P_c of the PVAc with different molecular structure and molecular weight in scCO₂ were determined at a concentration of 0.2 wt % PVAc in CO₂ and 35 °C. The polymer concentration was chosen to compare with other PVAc/CO₂ studies [24, 25, 29] and a large amount of polymer loading needed much higher dissolving pressure that would exceed the capacity of our instrumentation. Figures 4a and 4b show the P_c of the PVAc with end group and end-removed PVAc as a function of the molecular weight, respectively. The M_n was varied from 1000 to 7000 g/mol. For the linear PVAc, the P_c increases with increasing the M_n , which is consistent with the literature [29]. However, the P_c versus M_n curves of the multi-armed PVAc followed a different trend. For both 3-armed and 4-armed PVAc, with the increase of M_n , the P_c first decreased, and then increased, which exists a lowest pressure at a given M_n . The M_n value corresponding to the lowest pressure depended on the molecular chain structure of the PVAc and was in the range

of 3000-4000 g/mol. In addition, the P_c declined when increasing the number of arms at high M_n , whereas increased at low M_n , which indicated the polymer arms were negative to decrease the P_c when M_n was kept at a low level. In other PVAc/CO₂ studies, Cooper et al. [29] also found that linear PVAc with a M_n about 1700 g/mol had a lower P_c than the 3-armed PVAc, while Tan et al. [33] claimed that the PVAc with more arms had lower P_c at about 3500 g/mol. The trends of their results looked contradictory, but had a basic agreement with the results in this work. In addition, the distinction of the trends should be due to the effect of M_n on the CO₂-philicity of the PVAc with multi-armed structure. The existence of the minimum value in the cloud point curve of multi-armed PVAc indicated that there were some unfavorable factors such as strong polymer-polymer interactions leading to an increase of the P_c compared with the linear PVAc at low M_n . To understand the observed solubility behavior of PVAc with different molecular weight and structure, a respective contributions of polymer-solvent and polymer-polymer interactions were evaluated in the section 4.3.

Figure 4 also shows that the P_c of the end-removed linear, 3-armed, 4-armed PVAc in scCO₂ are lower than those of the corresponding end group non-removed ones. For example, the removal of the end group of the 3-armed PVAc ($M_n = 4099$ g/mol) would result in P_c decrease from 27.0 to 24.1 MPa. Especially for PVAc at low M_n , the end group effect would be more significant reflected by a large decline of P_c after removing the end groups. These results indicated that the thiocarbonylthio groups did harm to the CO₂-philicity of the polymer. Thus, the removal of these groups would be helpful to improve the solubility of the PVAc in scCO₂.

Figure 4. Effect of the molecular weight on the cloud point pressures of (a) PVAc with different molecular structure and (b) the products obtained by their reduction of end groups. The lines only indicated the trend. (Δ and $\bullet$ were measured at 30 °C with a polymer amount of 0.1 g in a 10 mL cell, and other data points were all measured at 35 °C with a concentration of 0.2 wt% CO₂).

4.3. Models and simulations

4.3.1. Polymer Chain-CO₂ Interaction

In a polymer/CO₂ system, the polymer-CO₂ and polymer-polymer interactions exist simultaneously and affect each other. In order to exclude the impact of polymer-polymer interaction and offer a clearer understanding on the effect of the multi-armed structure on the interaction between polymer and CO₂, the simulation box containing only one polymer chain and 1000 CO₂ molecules (systems 6 to 10 in Table 1) was introduced to evaluate the polymer-CO₂ interaction by using MD calculations.

Table 3. Interaction energy between a single polymer chain and 1000 CO₂ molecules. (kJ/mol)

System	E_{inter}	E_{vdW}	E_{electro}	$E_{\text{inter-single}}$
PVAc ₃₀	-673.5	-535.0	-138.6	-22.5
PVAc ₃₀₋₃	-688.6	-542.0	-146.6	-23.0
PVAc ₃₀₋₄	-707.4	-570.0	-137.4	-23.6

PVAc ₃₈	-819.5	-668.0	-151.6	-21.6
PVAc ₃₈₋₃	-846.8	-686.0	-160.7	-22.3
PVAc ₃₈₋₄	-889.5	-701.4	-188.1	-23.4
PVAc ₅₀	-1169.5	-915.0	-254.6	-23.4
PVAc ₅₀₋₃	-1194.4	-921.7	-272.8	-23.9
PVAc ₅₀₋₄	-1210.1	-951.6	-258.5	-24.2
PVAc ₆₀	-1472.6	-1122.1	-350.5	-24.5
PVAc ₆₀₋₃	-1505.7	-1182.5	-323.1	-25.1
PVAc ₆₀₋₄	-1621.1	-1220.6	-400.5	-27.0
PVAc ₇₅	-1730.3	-1209.0	-521.3	-23.1
PVAc ₇₅₋₃	-1807.5	-1312.7	-494.8	-24.1
PVAc ₇₅₋₄	-1839.6	-1338.5	-501.1	-24.5

The polymer chain-CO₂ interaction can be quantitatively evaluated through calculation of the binding energies between the polymer chain and CO₂. The binding energies can reflect the binding strength between the polymer chain and CO₂. The binding energy in a polymer chain-CO₂ system was calculated from the energy analysis of the simulation results in Forcite program, expressed as follows:

$$E_{\text{inter}} = -E_{\text{binding}} = E_{\text{chain/CO}_2} - (E_{\text{chain}} + E_{\text{CO}_2}) \quad (1)$$

where E_{inter} and E_{binding} referred to the interaction energy and the binding energy between CO₂ and a single polymer chain. $E_{\text{chain/CO}_2}$ represented the energy of polymer chain/CO₂ system. E_{CO_2} and E_{chain} were the energies of CO₂ and the polymer chain in the system, respectively. Table 3 shows the calculated results of the interaction energy between CO₂ and the polymer chains with different M_n and molecular structure. More details about the simulated results of $E_{\text{chain/CO}_2}$, E_{CO_2} and E_{chain} can be found in Table S2 of the Supporting Information.

The interaction energies between CO₂ and multi-armed PVAc chains were stronger than

that of linear PVAc chain with the same M_n , and the interaction energy between CO₂ and the 4-armed structures was the largest at the same M_n , indicating that the multi-armed structure was favorable to enhance the interaction and compatibility between CO₂ and polymer. The interaction energy was attributed to two kinds of interaction, comprising van der Waals force and electrostatic force, denoted as E_{vdW} and E_{electro} , respectively. The van der Waals energy was predominant interaction between CO₂ and polymer, as illustrated in Table 3, and the variation tendency of the E_{vdW} was consistent with that of E_{inter} . The E_{inter} was enhanced with the increase of M_n due to the more interaction point between CO₂ and the polymer with increased repeat units. The average interaction energy between CO₂ and each repeating unit in the chain, denoted as $E_{\text{inter-single}}$, was also calculated from the E_{inter} divided by the number of repeating units. The $E_{\text{inter-single}}$ was almost in the range of 22-27 kJ/mol and changed little with different M_n . In our previous work [42], the interaction energy between VAc dimer and CO₂ was studied by using the *ab initio* method. In the stable configuration, the carbon atom of CO₂ was placed between carbonyl oxygen in one repeat unit and ether oxygen in the other repeat unit, and the interaction energy was 21.3 kJ/mol. The results of $E_{\text{inter-single}}$ were all slightly larger than the interaction energy between VAc dimer and a CO₂ molecule calculated by the *ab initio* method, which was reasonable since more CO₂ molecules could place in more different positions near the polymer chain and cause stronger interaction between CO₂ and polymer chain in MD simulations. In conclusion, the van der Waals interaction dominates the interaction of polymer chain/CO₂ system, and the multi-armed structure can enhance the interaction between CO₂ and polymer chain, which is always favorable to the compatibility

between polymer and CO₂.

4.3.2. Polymer-Polymer Interaction

Besides the polymer-CO₂ interactions, the polymer-polymer interaction has strong influence on the compatibility of polymer with CO₂. Moderate polymer-polymer interaction is essential for its dissolution in CO₂. The cohesive energy (E_{coh}) was an important criterion to evaluate the inter-molecular force of polymer. CED, denoted as e_{coh} , is the ratio between E_{coh} and the volume of polymer, V , according to:

$$e_{\text{coh}} = E_{\text{coh}} / V \quad (2)$$

Additionally, the Hildebrand solubility parameter is described as the square root of CED, expressed as follows:

$$\delta = \sqrt{e_{\text{coh}}} = \sqrt{E_{\text{coh}} / V} \quad (3)$$

where δ represented the solubility parameter. In general, the value of CED could characterize quantitatively to describe the intermolecular interaction between polymer chains. To investigate the effect of molecular structure and M_n on the CED and solubility parameter of polymer, linear and multi-armed PVAc system with different M_n were simulated by using MD method. There was different number of polymer chains but similar total repeat units in the simulation boxes. The number of repeat units and chains in different cases was listed as systems 1 to 5 in Table 1.

Figure 5 shows the calculated results of CED and solubility parameter analyzing from the trajectories of final 50 ps in MD simulations. The more details about the data of CED and

density are listed in Table S3 of the Supporting Information. In general, the number of monomer repeat units of polymer chain had a significant effect on the CED and solubility parameter, especially at the low M_n . In the M_n range in this work, the e_{coh} and δ decreased slowly with increasing the M_n of PVAc with different molecular structures, which is consistent with the relationship between the calculated solubility parameter and the number of repeat units for some other polymers [48, 49]. The e_{coh} of the 4-armed PVAc was larger than those of the 3-armed PVAc and linear PVAc at the M_n of 2580 g/mol. The multi-armed structure enhanced intermolecular interactions between polymer chains, which might be caused by the increase of end groups. The difference in e_{coh} between different molecular structures was significantly reduced at the M_n of 4300 g/mol. In contrast, the e_{coh} of the linear PVAc was greater than that of the multi-armed PVAc when the M_n of the polymer was increased to 5000 g/mol. Multi-armed structure led to more moderate polymer-polymer interaction when the chain length of polymer reached an enough size. It could be attributed to the reduction of chain entanglement in the presence of branched chains.

According to the principle of "like dissolves like", the polymer with a similar solubility parameter to CO₂, tends to have a good compatibility with CO₂. In general, the δ values of polymers are always larger than that of CO₂. The δ value of CO₂ was 13.10 at 20 MPa and 35°C, calculated by MD simulations in our previous work [43]. As shown in Figure 5(b), it can be seen that the δ of the linear PVAc was closer to that of CO₂ at the M_n of 2580 g/mol while the δ of the 4-armed PVAc was closer to that of CO₂ at the M_n larger than 5000 g/mol, indicating that linear PVAc had a better compatibility at 2580 g/mol but had a poorer

compatibility at above 5000 g/mol with CO₂ than the multi-armed PVAc. From the viewpoint of PVAc chain self-interaction, the multi-armed structure had different effects on the compatibility with CO₂ at different M_n range. At the high M_n , the multi-armed PVAc should be a better candidate for enhancing the solubility and decrease the P_c in CO₂.

Figure 5. Effect of M_n on simulated CED and solubility parameter of PVAc with different structures.

The contribution of polymer-polymer interactions was also evaluated from surface tension which was commonly measured with sessile drop measurements. The surface tensions of the polymers were obtained by water contact angle through the empirical formula proposed by Li and Neumann [50] and the experimental method was the same as Girard et al. [28] (see Table S1 in the Supporting Information). The larger surface tension indicated the stronger polymer-polymer interaction [13, 23]. As shown in Figure 6, increase in the molecular weight would result in a decline of surface tension at the molecular weight between 1000 and 7000 g/mol. The surface tension of the multi-armed PVAc decreased more significantly with increasing the molecular weight than that of the linear PVAc. At low M_n , the surface tension of the multi-armed PVAc was higher than that of the linear one, indicating that the

polymer-polymer interactions of multi-armed PVAc were stronger than that of the linear one and might weaken the CO₂-philicity of multi-armed PVAc. However, the polymer-polymer interactions of multi-armed PVAc sharply reduced with further increasing the molecular weight comparing to linear PVAc, which might lead to the enhancement of CO₂-philicity. The results were basically consistent with the simulation results and evidenced that the important impact of polymer-polymer interactions on the polymer CO₂-philicity.

Figure 6. The surface tension of PVAc with different molecular structure and molecular weight.

4.3.3. Flory-Huggins Interaction Parameter

Actually, the polymer-CO₂ interaction and polymer-polymer interaction occur simultaneously and cannot be separated from each other in the real polymer/CO₂ systems. In order to provide a complete understanding of the compatibility between polymer and CO₂, the Flory-Huggins interaction parameter was introduced to estimate the CO₂-philicity of polymers. This parameter, denoted as χ_{12} , contained simultaneously the factor of polymer-CO₂ interaction and that of polymer-polymer interaction. The χ_{12} could be calculated from the following equation:

$$\chi_{12} = \left(\frac{\Delta E_{\text{mix}}}{RT\phi_A\phi_B} \right) V_m \quad (4)$$

where R and T referred to the molar gas constant and the temperature in Kelvin, respectively. V_m was the reference mole volume. ϕ_A and ϕ_B were the volume fractions of polymer and CO_2 in the polymer/ CO_2 system, respectively. ΔE_{mix} represented the mixing energy between polymer and CO_2 , which could be evaluated by the following equation:

$$\Delta E_{\text{mix}} = \phi_A e_{\text{coh,A}} + \phi_B e_{\text{coh,B}} - e_{\text{coh,mix}} \quad (5)$$

where $e_{\text{coh,A}}$ and $e_{\text{coh,B}}$ were the CED of polymer and CO_2 , respectively. $e_{\text{coh,mix}}$ represented the CED of the polymer/ CO_2 system, and the data of polymer/ CO_2 system density were listed in Table S4 of the Supporting Information. The critical value of miscibility criterion χ_c can be calculated by eq 6:

$$\chi_c = \frac{1}{2} \left(1 + \frac{1}{\sqrt{n}} \right)^2 \quad (6)$$

where n was the number of repeat units in the polymer chain. When χ_{12} of the mixture was smaller than χ_c , the system is considered to be miscible well. For the same number of repeat units, the smaller χ_{12} suggested the more miscible binary system. The critical value of miscibility, χ_c , was all ranging from 0.62 to 0.70 due to the number of repeat units in this work.

Figure 7 illustrates the values of χ_{12} between CO_2 and PVAc with different M_n and different structures calculated by using eq.(4). The results showed that all the χ_{12} of the PVAc/ CO_2 systems were higher than the critical value, indicating a poor compatibility between PVAc and CO_2 , which was consistent with the fact that CO_2 was a weak solvent for

polymers. By comparing the χ_{12} in these PVAc/CO₂ systems, it could be found that the χ_{12} of linear PVAc was lower than that of the multi-armed PVAc systems at 2580 g/mol, proposing that multi-armed PVAc was not a good choice to enhance the compatibility of PVAc with CO₂, which agreed well with the experiment results of the P_c in CO₂. At the small M_n , the difference of CED is significant between different molecular chain structure, and the CED was the main driving force deciding the CO₂-philicity. With increasing the M_n , the difference of CED reduced between different molecular chain structures, and the difference of χ_{12} was also smaller. When the M_n was larger than 5000 g/mol, the χ_{12} of linear PVAc was larger than that of the multi-armed PVAc systems, indicating that the multi-armed PVAc was a better choice for the dissolution of PVAc in CO₂. The conclusion also agreed well with the experiment results. From the simulation results, at high M_n , the multi-armed structure was favorable to the CO₂-philicity due to the synergistic effect of more moderate polymer-polymer interaction and stronger polymer-CO₂ interaction.

Figure 7. Flory-Huggins interaction parameter between CO₂ and PVAc with different M_n and different structures

4.3.4. Radial distribution functions

To obtain a more thorough understanding of the polymer-polymer and polymer-CO₂ interactions in the polymer/CO₂ system, radial distribution function, denoted as $g(r)$, was introduced to analyze the simulation result after MD calculations. This function describes how density varies as a function of distance from a reference particle and reflects the micro-structural characteristics, which is a useful analysis method in the structural characterizations to study the regularity of specific interactions between the particles (atoms, molecules, colloids, etc.) in the system. It was defined as:

$$g_{AB}(r) = \frac{\langle n_{AB}(r) \rangle}{\rho_{AB} \cdot 4\pi r^2 \cdot \Delta r} \quad (7)$$

where $g_{AB}(r)$ represented the radial distribution function, and the subscripts A and B referred to two kinds of particles. $\langle n_{AB}(r) \rangle$ was the average number of atom pairs in a distance interval Δr between r and $r+\Delta r$. ρ_{AB} referred to the density of atom pairs of AB. The inter-molecular $g(r)$ was related to the correlations of molecular arrangement between different molecules or chains to evaluate the compatibility between polymer and CO₂ [51].

The $g(r)$ of intermolecular carbon atomic pairs for PVAc chains with different molecular structures are plotted in Figure 8. Here we only show the $g(r)$ of pure polymer systems, system 1, 3 and 5 in Table 1, corresponding to the M_n of 2580, 4300 and 6450 g/mol. As shown in Figure 8, no sharp peaks were observed in the curves of $g(r)$, indicating that the C atoms of two different polymer chains were not systematically arranged in order at a r distance from one another, which agreed well with the amorphous structure of PVAc. At the

M_n of 2580 g/mol, the $g(r)$ intensities of multi-armed PVAc were higher than that of linear PVAc on a same distance, indicating that the C atoms of multi-armed PVAc were more closely surrounded by other polymer chains. It was a strong indicator that the chain interactions of multi-armed PVAc, as well as the C-C atom pair interactions, were stronger at this M_n . However, the $g(r)$ curves had significant differences at the M_n of 6450 g/mol. The $g(r)$ values of linear PVAc were higher than that of multi-armed PVAc at a same distance, indicating that the polymer-polymer interaction of linear PVAc was stronger at this M_n . The results of $g(r)$ were also consistent with the tendency of CED calculated in MD simulations, which was self-consistent with the inherent logic of interaction between polymer chains.

Figure 8. Intermolecular distribution for the C-C pairs in PVAc with different M_n and different

structures.(a)2580g/mol; (b) 4300g/mol; (c) 6450g/mol.

The $g(r)$ of intermolecular C-C atom pairs between polymer and CO₂ were also calculated from the simulation results of the systems 11, 13 and 15 in Table 1. As shown in Figure 9, at the M_n of 2580 g/mol, the $g(r)$ of C-C atom pairs between CO₂ and linear PVAc were slightly higher than that between CO₂ and multi-armed PVAc on a same distance. It was proposed that the C atoms of CO₂ could contact linear PVAc more closely due to the weaker contact between polymer chains of linear PVAc. At the M_n of 4300 g/mol, the differences of $g(r)$ were very small in PVAc with different molecular structures. However, at the M_n of 6450 g/mol, the $g(r)$ values of C-C atom pairs between CO₂ and linear PVAc were lower than that between CO₂ and multi-armed PVAc on a same distance. The difference of tendency in $g(r)$ could also be attributed to the polymer-polymer interactions caused by the different molecular structures at different M_n . Thus, with different M_n , there was a big difference in the effect of polymer molecular structures on the CO₂-philicity. The comparisons of $g(r)$ values offered a deeper understanding on the interactions of polymer/CO₂ systems at the molecular level. Within a certain range of the M_n , the appropriate molecular structure could be selected to enhance the CO₂-philicity of PVAc.

Figure 9. Intermolecular distribution for the C-C pairs between polymer chains and CO₂. (a) 2580 g/mol; (b) 4300 g/mol; (c) 6450 g/mol.

5. CONCLUSION

The linear, 3-armed and 4-armed R-core PVAc was synthesized by RAFT polymerization with well-defined M_n distributions, and then the corresponding xanthate groups were removed. The CO₂-philicity of the multi-armed PVAc was found to be inferior to that of the linear one at low M_n . With increasing the M_n from 1000 to 7000 g/mol, the P_c of both 3-armed and 4-armed PVAc first decreased, reached a minimum at a given M_n , which was lower than that of the linear PVAc, and then increased. It was different from the variation trend of the P_c of

linear PVAc versus M_n . In addition, removal of the xanthate groups could effectively enhance the CO₂-philicity of PVAc, especially at low M_n .

The MD simulations proposed that the multi-armed structures could enhance the interaction between CO₂ and polymer. However, they had different effects on the CED of polymer at different M_n range. The CED of the multi-armed PVAc was larger than that of the linear one at the low M_n while the trend of CED was the opposite at the high M_n . Meanwhile, the variation trend of calculated CED versus M_n had a good agreement with that of the surface tension versus M_n , reflecting the polymer-polymer interaction. At low M_n , the polymer-polymer interaction was the main driving force to lead the better CO₂-philicity of linear PVAc while the multi-armed structure enhanced the CO₂-philicity due to the synergistic effect of moderate polymer-polymer interaction and large polymer-CO₂ interaction at the high M_n . The $g(r)$ of PVAc/CO₂ systems with different M_n also confirmed that the tendency of polymer self-interaction and CO₂-philicity of PVAc were difference caused by the different molecular structures at different M_n , which offered a deeper understanding on the interactions of polymer/CO₂ systems at the molecular level. Within a certain range of the M_n , the appropriate molecular structure could be selected to enhance the CO₂-philicity of PVAc.

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Captions

Scheme 1. Synthesis of 3-armed and 4-armed R-core Star Xanthate Agents.

Figure 1. ^1H NMR spectra of (a) 4-armed R-core Star Xanthate agent and corresponding (b) 4-armed R-core star PVAc and (c) the end-removed product.

Figure 2. Evolution of the molecular weight and molecular weight distribution with conversion for polymerization with two 3-armed and 4-armed RAFT agents of VAc at 60 °C. The lines only indicate the trend.

Figure 3. Gel permeation chromatograms for two samples of (a) 3-armed PVAc and (b) 4-armed PVAc and the products obtained by their reduction with dilauroylperoxide in 2-propanol (80 °C/6 h). Peak molecular weights are exhibited on the chromatograms.

Figure 4. Effect of the molecular weight on the cloud point pressures of (a) PVAc with different molecular structure and (b) the products obtained by their reduction of end groups. The lines only indicated the trend. ($\triangle$ and $\bullet$ were measured at 30 °C with a polymer amount of 0.1 g in a 10 mL cell, and other data points were all measured at 35 °C with a concentration of 0.2 wt% CO_2).

Figure 5. Effect of M_n on simulated CED and solubility parameter of PVAc with different structures.

Figure 6. The surface tension of PVAc with different molecular structure and molecular weight.

Figure 7. Flory-Huggins interaction parameter between CO_2 and PVAc with different M_n and different structures

Figure 8. Intermolecular distribution for the C-C pairs in PVAc with different M_n and different structures. (a) 2580 g/mol; (b) 4300 g/mol; (c) 6450 g/mol.

Figure 9. Intermolecular distribution for the C-C pairs between polymer chains and CO_2 . (a) 2580 g/mol; (b) 4300 g/mol; (c) 6450 g/mol.

Table 1. Systems with different compositions of PVAc and CO_2 in MD simulations

Table 2. Experiment result for the synthesis of linear and multi-armed PVAc

Table 3. Interaction energy between a single polymer chain and 1000 CO_2 molecules. (kJ/mol)

Graphic Abstract