Journal of Southeast University (English Edition) Vol. 35, No. 2, pp. 264 − 268 June 2019 ISSN 1003—7985

Synthesis of poly (vinyl acetate) oligomers and their phase behavior in supercritical carbon dioxide

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Abstract: Three poly (vinyl acetate) (PVAc) oligomers with controlled molecular weight and narrow molecular distribution are synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. The effects of the reaction temperature and the added amount of initiator of the PVAc polymerization are discussed. In addition, the phase behavior of the prepared PVAc in pressured CO_2 is determined via the cloud point method. The results indicate that the cloud point of PVAc increases with the increase in the molecular weight, the PVAc concentration, and the temperature. The cloud point pressures for the PVAc mass concentration of 0.12 % with the molecular weight of 1 550, 2 120, and 2 960 g/mol are 13.48, 13.83 and 15.43 MPa, respectively, at the temperature of 35 ℃. It reveals that the solubility of PVAc in $ScCO_2$ at relatively low pressure is remarkably limited.

Key words: poly (vinyl acetate); polymerization; supercritical carbon dioxide; cloud point pressure; CO_2-philic polymer

DOI: 10.3969/j.issn.1003 − 7985.2019.02.018

Supercritical carbon dioxide ($ScCO_2$) is believed to be an environmentally-benign solvent due to its advantages such as being non-toxic, non-flammable, cheap, having a relatively low critical temperature, and pressure[1]. It has been widely used in the preparation of drug delivery systems[2-3]. In addition, non-toxic and biodegradable polymers are also regarded as suitable materials for drug delivery systems. Unfortunately, the solubility of most of the polymers is poor in $ScCO_2$ even at very high pressure, which limits their application for the processes based on $ScCO_2$.

Some CO_2-philic hydrocarbon polymers so far have been successfully synthesized. Girard et al.[4] introduced the developments in CO_2-philic polymers and summarized their structure-property relationships. Due to its non-toxic and biodegradable properties, poly (vinyl acetate) is regarded as one of the most promising CO_2-philic polymers for the preparation of the drug delivery system using $ScCO_2$[5]. The phase behavior of PVAc samples with different molecular weights or architectures in CO_2 has been determined[6-11]. The results show that the molecular weight of PVAc might be the most important factor for solubility in $ScCO_2$, which decreases with the increasing molecular weight. Recently, we designed a new process for the preparation of the drug-loaded micelles by the self-assembly of the amphiphilic block polymer with a CO_2-philic block and a hydrophilic one. In this system, water acts as a continuous phase, and $ScCO_2$ is a dispersed phase[12]. PVAc with a linear structure which is believed to be a suitable CO_2-philic block for the process. Due to the expensive cost of the equipment and the risk of high-pressure processes, the processes at a relatively lower pressure are welcome. However, the solubility data of PVAc with relatively low molecular weight in $ScCO_2$ under low pressures are scarce, resulting in the design of the $ScCO_2$ processes with PVAc at relatively low pressures being difficult. Therefore, the determination of the solubility of PVAc in $ScCO_2$ under low pressure is necessary.

In this study, the PVAc oligomers with a narrow molecular distribution are synthesized via reversible addition-fragmentation chain transfer (RAFT) radical polymerization, and the kinetic analysis of the polymerization is carried out. In addition, the phase behavior of three PVAc oligomers with low molecular weights in $ScCO_2$ under relatively low pressure is determined and discussed. These results can be used to develop the processes based on the $ScCO_2$ and PVAc at relatively low pressures.

1 Experimental

1.1 Materials

Vinyl acetate with a purity of 97% is purchased from Sinopharm Chemical Reagent Co. Ltd. and used before passing through an alumina column to remove the inhibitor. 2, 2-Azobisisobutyronitrile (AIBN) was obtained from Aldrich and used before recrystallizing three times using ethanol. CO_2(99.99% purity) is supplied by Nanjing Special Gases factory Co. Ltd. Other reagents are

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Received 2018-11-03, **Revised** 2019-04-10.

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Foundation items: The Natural Science Foundation of Jiangsu Province (No. BK20130602), the Applied Basic Research Program of Suzhou (No. SYG201836), the Project of the Collaborative Innovation Center of Suzhou Nano Science and Technology.

Citation: Jiao Zhen, Song Junying, Fan Wenjing, et al. Synthesis of poly (vinyl acetate) oligomers and their phase behavior in supercritical carbon dioxide[J]. Journal of Southeast University (English Edition), 2019, 35(2): 264 − 268. DOI: 10.3969/j.issn.1003 − 7985.2019.02.018.

commercially available and are used as received.

1.2 Synthesis of PVAc

The chain transfer agents for RAFT polymerization (e. g. (S)-2-(Ethyl propionate)-(O-ethyl xanthate) are synthesized in accordance with Ref. [13]. The yield is 72%, and the structure is verified using FTIR and ^{1}HNMR.

All of the polymers in this study are prepared according to the following process. As a typical RAFT polymerization, vinyl acetate (8.600 g, 100 mmoL), AIBN (0.033 g, 0.2 mmoL) and (S)-2-(ethyl propionate)-(O-ethyl xanthate) (0.222 g, 1 mmoL) are added to a round-bottom flask with 20 mL ethanol as the solvent. After the mixture is repeatedly degassed and filled with dry nitrogen three times, the reaction proceeds under stirring for several hours. Then, the solvent is removed by a rotary evaporator, and the residual polymerization mixture is dissolved in tetrahydrofuran and precipitated using hexanes(200 mL). The purification process is repeated twice, and the final product is dried under vacuum at room temperature.

The structure of the prepared PVAc is determined using FTIR and ^{1}HNMR. The molecular weight and PDI of the polymers are measured by GPC. Considering that the solubility of PVAc in ScCO$_2$ is dependent on the molecular weight[14], the preparation of PVAc with the target molecular weight and a narrow molecular distribution is necessary. Therefore, the effects of reaction temperature and the amount of initiator on the PVAc polymerization are discussed.

1.3 Phase behavior determination of PVAc in CO$_2$

The phase behavior of PVAc in ScCO$_2$ is determined via the cloud point method[15]. During the experiment, PVAc is added to a vessel. Then, the vessel is put into the water bath and connected to the pressure gauge. After that, carbon dioxide is introduced into the vessel very slowly using the high-pressure pump until the PVAc dissolves under magnetic stirring. The added amount of carbon dioxide can be calculated by the temperature, the pressure and the volume of the vessel. The pressure inside the vessel is decreased very slowly by gradually increasing the volume of the cell via a screw rotating upward until the cloud point is observed. The cloud point demonstrates that the solute in this system begins to dissolve out, and the pressure at this point is called the cloud point pressure. Each experiment is repeated three times and the average value is calculated.

2 Results and Discussion

2.1 Synthesis of PVAc

PVAc is prepared via the reaction of vinyl acetate, AIBN and the chain transfer agents. The structure is confirmed by FTIR and ^{1}HNMR[6]. Fig. 1 shows the time-conversion curves of the polymerization at two temperatures (i. e., 50 and 60 ℃) with the additional vinyl acetate, CTA, and AIBN of 100, 1, and 0.5 mmol, respectively. The result indicates that the process is sensitive to the temperature. The rate of the vinyl acetate conversion at 60 ℃ is much faster than that at 50 ℃. The reason might be due to the decomposition rate of initiator decrease during the chain initiation process with the decreasing temperature[16].

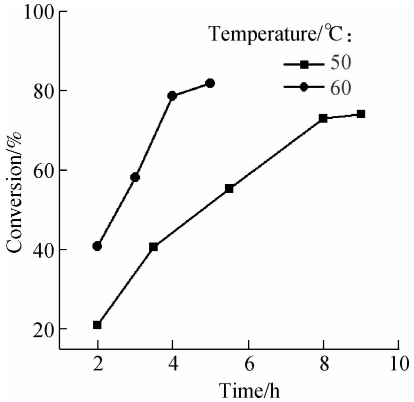
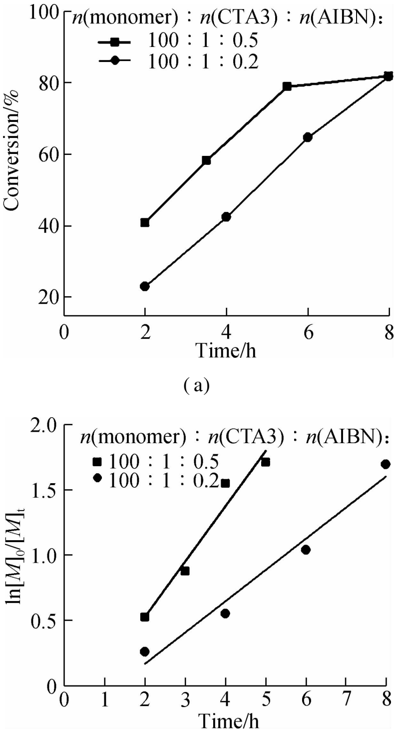


Fig. 1 The plot of the reaction time vs. the conversion for the polymerization of PVAc with the additional vinyl acetate, CTA, and AIBN of 100, 1, and 0.5 mmol, respectively, at the temperatures of 50 and 60 ℃

Fig. 2(a) shows the plots of the reaction time vs. the conversion at different ratios of initiator addition and the



(a)

(b)

Fig. 2 Effects of the reaction temperature and the added amount of initiator of the RAFT polymerization of VAc at 60 ℃. (a) Plot of the reaction time vs. the conversion at different ratios of initiators; (b) Plot of time vs. $\ln[M]_0/[M]_t$ at different ratios of initiators temperature of 60 ℃. It indicates that the initiator concentration plays a crucial role in the polymerization. The increasing initiator addition effectively accelerates the reaction rate. Fig. 2(b) shows the plots of the reaction time vs. $\ln[M]_0/[M]_t$ at different ratios of initiator addition, where $[M]_0/[M]_t$ is the mole ratio of VAc at the initial time and the reaction period. It indicates that $\ln[M]_0/[M]_t$ is linear with the polymerization time. The result is consistent with the characteristics of living polymerization[17].

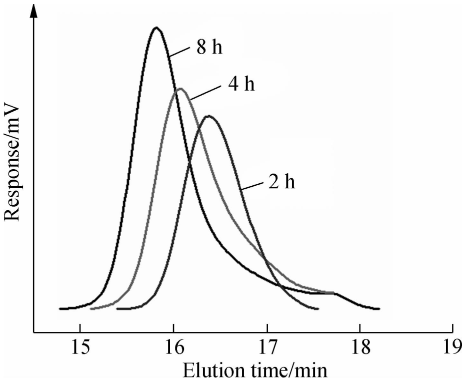


Fig. 3 GPC traces for the PVAc with reaction time at 2, 4 and 8 h

Fig. 3 displays the GPC traces for the PVAc polymerized at 60 ℃ under different reaction times. The reaction is carried out at the feeding ratios of VAc, CTA, and AIBN of 100, 1 and 0.2 mmol, respectively. It can be found that the peak of GPC gradually becomes narrow with the extension time. This means that the reaction time can encourage the formation of a narrow molecular weight distribution of PVAc. This result is also consistent with the characteristics of living polymerization[17].

Tab. 1 shows the molecular weight of PVAc and their PDI at different feeding ratios after the reaction is continued for 4 h under 60 ℃. The results indicate that a series of different molecular polymers with narrow molecular weight distribution are obtained. Moreover, the molecular weight is increased with the enhancing initial VAc addition.

Tab. 1 Polymerization of PVAc at different VAc feeding mole ratios

Run	$M_{\mathrm{VAc}}:M_{\mathrm{CTA}}:M_{\mathrm{AIBN}}$	Molecular weight/ ($\mathrm{g \cdot mol^{-1}}$)	Conversion/ %	PDI
1	25:1:0.2	1 020	61.3	1.22
2	50:1:0.2	2 320	60.8	1.13
3	100:1:0.2	2 960	78.7	1.14

Note: $M_{\mathrm{VAc}}:M_{\mathrm{CTA}}:M_{\mathrm{AIBN}}$ is the mole feeding ratio of VAc, CTA and AIBN.

2.2 Phase behavior of PVAc oligomers in CO_2

The PVAc samples used for the phase behavior experiments are prepared with the additional mole ratio of VAc: CTA: AIBN to be 100 : 1 : 0.2 at the temperature of 60 ℃ and different reaction times. The cloud point pressures of the samples are determined with the concentration of 0.03%, 0.06% and 0.12% in mass fraction at the temperatures of 25, 35, 40 and 45 ℃, respectively. The results listed in Tab. 2 indicate that the cloud point pressure can be effectively reduced by the lower molecular weight. The same conclusion is reported in Refs. [8 - 11]. However, the cloud point pressures of PVAc-1 (1 550 g/mol) are slightly higher than that of PVAc-2 (2 120 g/mol) at 45 ℃ with the mass concentrations of 0.06 % and 0.12%. The reason might be due to the wider PDI of PVAc-1[9]. The final group may have an influence on the solubility of PVAc in $ScCO_2$. However, due to its very little proportion in the polymer samples, the solubility of PVAc is decided by the main chain of the polymer.

Tab. 2 Phase behavior of PVAc samples in CO_2

Sample	Mass concentration/%	Molecular weight/ ($\mathrm{g \cdot mol^{-1}}$)	PDI	Cloud point pressure/MPa			
				25 ℃[a]	35 ℃	40 ℃	45 ℃
PVAc-1	0.03	1 550	1.17	8.22	10.63	12.07	13.49
	0.06	1 550	1.17	8.61	11.79	13.43	14.72
	0.12	1 550	1.17	9.43	13.48	14.82	15.47
PVAc-2	0.03	2 120	1.32	8.99	12.21	13.18	13.92
	0.06	2 120	1.32	9.76	12.39	13.79	14.37
	0.12	2 120	1.32	10.57	13.83	14.62	15.14
PVAc-3	0.03	2 960	1.14	9.43	14.04	15.36	—[b]
	0.06	2 960	1.14	10.42	15.01	—[b]	—[b]
	0.12	2 960	1.14	10.75	15.43	—[b]	—[b]

Notes: [a] means the phase of CO_2 is liquid at this temperature; [b] means partial solubility at the pressure of 16 MPa.

The experimental results also illustrate that the temperature is important for the solubility in $ScCO_2$. The cloud point pressure is increased with the increase in temperatures, indicating that the solubility of PVAc in $ScCO_2$ is generally less at a higher temperature. Therefore, higher pressure is needed to dissolve the PVAc with increasing temperatures[13]. The cloud point pressures for 0.12% PVAc with the molecular weight of 1 550, 2 120, and 2 960 g/mol are 13.48, 13.83 and 15.43 MPa at the temperature of 35 ℃, indicating that the solubility of PVAc in $ScCO_2$ at a relatively low pressure seems remarkably limited.

Only little solubility data of PVAc with a low molecular weight (lower than 3 000 g/mol) in CO_2 have been reported. For example, Rindfleisch et al.[7] observed that the cloud point pressures are 13.6, 20.8 and 37.4 MPa for the PVAc mass concentration of 5% with the molecular weight of 780, 850, and 2 060 g/mol at 25 ℃, respectively. Zhang et al.[9] determined the cloud point pressures of PVAc with the molecular weight of 1 320, 2 030, 2 400 and 2 750 g/mol in CO_2 at the mass/volume concentration of 0.15 %. They were 9.0, 9.6, 10.9 and 12.2 MPa at 25 ℃ as well as 18.1, 19.4, 20.8 and 22.2 MPa at 50 ℃. These results also show that the solubility of PVAc with low molecular weight is limited. In brief, even for the PVAc samples with very low molecular weight, their solubility in $ScCO_2$ is still limited compared to the fluorinated polyolefins (e.g., the cloud point pressure is 12.5 MPa for the perfluoropolyether (PFPE) with the mass concentration of 5% and the molecular weight of 13 kg/mol at 22 ℃)[16]. Therefore, the developments for CO_2-philic hydrocarbon polymers are still necessary.

3 Conclusion

1) The PVAc oligomers with narrow molecular distribution are synthesized by the RAFT polymerization using (S)-2-(ethyl propionate)-(O-ethyl xanthate) as the chain transfer agent in this study. The polymerization kinetics study shows that the process is consistent with the characteristics of living polymerization.

2) The cloud point pressures of PVAc with the molecular weight of 1 550, 2 120, and 2 960 g/mol are determined at the temperature of 25, 35, 40 and 45 ℃, respectively. The experimental results show that the cloud point pressure of PVAc increases with the increase in the molecular weight, the PVAc concentration, and the temperature.

3) The solubility of PVAc in $ScCO_2$ at a low pressure is remarkably limited. These results can be used to develop the process based on the $ScCO_2$ and PVAc at relatively low pressures.

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聚醋酸乙烯酯的合成及其在超临界二氧化碳中的相行为

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摘要:利用可逆加成-断裂链转移自由基聚合法制备了 3 个具有可控分子量和窄分子量分布的聚醋酸乙烯酯单聚物,并讨论了反应温度和引发剂加入量对聚合过程的影响.然后,通过浊点法测定了相对制得的聚合物在加压的二氧化碳中的相行为.结果表明,聚合物的浊点随着分子量、聚合物浓度和温度的增加而增大,在 0.12% 的质量浓度和 35 ℃温度下,分子量为 1 550, 2 120 和 2 960 g/mol 的聚醋酸乙烯酯的浊点压力分别为 13.48, 13.83 和 15.43 MPa,该结果表明聚醋酸乙烯酯在较低压力的超临界二氧化碳中溶解度十分有限.

关键词:聚醋酸乙烯酯; 聚合反应; 超临界二氧化碳; 浊点压力; 亲二氧化碳聚合物

中图分类号:O632.1; TQ013.1