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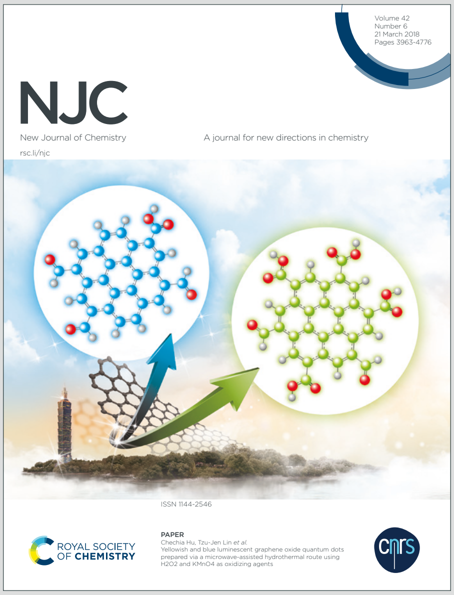

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ARTICLE

Investigation on modified polyether as efficient CO_2 thickener

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ABSTRACT: The development of new generation of carbon dioxide (CO_2) thickener is significant to improve carbon dioxide flooding technology. Here, copolymers based on epoxide heptamethyltrisiloxane and glycidyl phenyl ether are prepared, and their solubility and thickening ability in CO_2 are evaluated. The solubility of modified polyethers in CO_2 remarkably increases with the modification of heptamethyltrisiloxane and decreases with introducing phenyl glycidyl ether content. With incorporation of 18.4 mol% phenyl group in the copolymer, the copolymer exhibits greatly increased thickening effect while maitaining high solubility in CO_2. Implication of the present study for preparation of highly efficient CO_2 thickner is disscussed.

1. Introduction

Carbon dioxide enhanced oil recovery (CO_2-EOR) has attracted considerable attention due to improved oil recovery, good carbon dioxide capture and easily storage.[1-5] According to the report of 2014, about 152 projects of CO_2-EOR are in process in the world, and total oil production by CO_2-EOR in the world is up to $1470 \times 10^{14}\ t$.[6] However, there exists an unstable displacement front when oil is displaced by a less viscous fluid, resulting in an early breakthrough of displacing fluid and decreasing the sweep efficiency.[7] The major disadvantage of CO_2-EOR is the low viscosity of CO_2 (0.03-0.1 cp) compared to oil (typical 0.1-50 cp).[8,9] To fully optimize CO_2-EOR process and increasing the oil recovery rate, a direct approach is to increase the viscosity of CO_2.[10,11]

Recently, a large amount of research has been performed to identify or design thickeners for increasing the viscosity of CO_2. Utilizing polymers directly for improving the viscosity of CO_2 was firstly suggested by Heller et al.[12,13] The authors evaluated the solubility of abundant commercially available polymers in CO_2 and the ability of the polymers to increase CO_2 viscosity. Unfortunately, none has induced enough enhancement of CO_2 viscosity due to their low solubility. Subsequently, the design of the CO_2 soluble thickeners was paid more attention by Investigators. DeSimone et al. reported the high solubility of fluoropolymers in CO_2 and fluoroacrylate polymer was the first polymer that can successfully increase CO_2 viscosity at 2-8 fold without cosolvent, but need relatively high polymer concentration of 5-10 wt %.[14] To obtain more thickening effect (higher viscosity of CO_2 with less polymer content), Enick et al. suggested that CO_2 thickener should contain both CO_2-philic and CO_2-phobic moieties that contributed to solubility and thickness, respectively.[15] Fluoroacrylate-styrene random copolymers caused great increase of CO_2 viscosity via the π-π interaction between phenyl groups, 3-10 fold increase in viscosity with 1 wt % polymer loading at 25 °C and 34.5 MPa, and higher viscosity of CO_2 can be obtained with higher polymer loadings.[8,16,17] The author also found the small molecular compound such as semi-fluorinated trialkyltin fluorides, could thicken CO_2 3.3 fold at a concentration of 4 wt %.[18] However, these fluorinated thickeners are expensive and harmful to environment which restricted their application of industrial scale.

Thus, the following research was focused on the design of CO_2-philic nonfluorous polymers by thermodynamically improving the enthalpy and entropy of mixing. To date, CO_2-philic nonfluorous homopolymer identified mainly contain polysiloxanes (such as PDMS), vinyl homopolymer (such as poly(vinyl acetate) (PVAc), poly(methyl acrylate), poly(vinyl ethyl ether)), polyether (such as poly(propylene oxide) (PPO), poly(butylene oxide)) and polyester (such as poly(lactide)). Based on these polymers, a number of studies have been carried out to improve the solubility of polymers in CO_2. In terms of the mixing enthalpy, Destarac et al. enhanced poly(vinyl ester) solubility in CO_2 by decreasing the polymer-self interaction resulted from fluorinated side groups.[20] Based on PDMS with weak polymer intermolecular interactions and good chain flexibility, Enick et al. introduced CO_2-philic groups including carbonyl or acetoxy into PDMS to enhance PDMS-CO_2 interactions.[21] Beckman added carbonyl or acetoxy group to the backbone, side group, or end group of polyether to increase the polyether-CO_2 interaction.[22] For improving the mixing entropy, vinyl acetate was copolymerized with a bulky comonomer, dibutyl maleate[23], vinyl butyrate[24], vinyl octanoate[25] and vinyl pivalate to improve the chain flexibility or free volume of PVAc[26]. The characteristics of CO_2-philic polymers are considered as weak polymer-polymer interaction (prominent factor), strong polymer-CO_2 interaction (secondary factor) and high chain flexibility or free volume (third factor).[20,22,27,28] At present, the successful CO_2 thickener based on designed CO_2-philic nonfluorous polymer has not been reported, and preparation of inexpensive and effective CO_2 thickeners is still a challenge.

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In this paper, we chose polyether to synthesize polyether-based CO_2 thickener, due to its high CO_2-philicity stemmed from strong polymer-CO_2 interaction and high chain flexibility.[29,30] We recently reported that silicone unit could significantly decrease polyether self-interactions and enhance the solubility of polyether in CO_2.[31] Further, considering the effect of free volume on solubility, we incorporated heptamethyltrisiloxane as a bulky side group into polyether for simultaneously decreasing the polymer-polymer interaction along with increasing the free volume and consequently improve the solubility of polyether in CO_2. Then phenyl group was introduced into the modified polyether to induce intermolecular interactions and enhance the thickening ability of the polymer to CO_2. To investigate the relationship between structure and solution/thickening performances and to identify a more efficient thickener for CO_2, a series of modified polyethers with different contents of phenyl group were prepared and their physicochemical properties and solubility/thickening capacity were systematically discussed.

2. Experiment Section

2.1. Materials.

Allyl glycidyl ether (AGE), 1,1,1,3,5,5,5-heptamethyl trisiloxane (HMTS) and glycidyl phenyl ether (GPE) were purchased from J&K Scientific. Ethylene glycol (EG, 99.8%) and Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt~ 2% (Karstedt's Catalyst) were purchased from Sigma-Aldrich. Boron fluoride·ethyl ether complex (47-48% Boron fluoride) was obtained from TCI. Triethylamine, acetyl chloride and toluene were purchased from Beijing Chemical Works, and toluene was freshly distilled before use from a purple Na/benzophenone ketyl solution. Carbon dioxide (CO_2, 99.95%) was purchased from Changchun Juyang gas industry.

2.2. Methods.

Structure characterization. The nuclear magnetic resonance (NMR) spectra were conducted on a Bruker Avance III NMR spectrometer, operating at 400 MHz for the corresponding ^1H nuclei. Chemical shifts (in ppm) were recorded in $CDCl_3$ list as "residual internal $CHCl_3$ ($\delta = 7.26$)". The molecular weight of polymers was detected by Gel Permeation Chromatography (GPC) using a Malvern apparatus equipped with a VE 3580 refractive index detector thermostated and a set of three Malvern columns (T5000, T3000 and T1000) thermostated at 35 °C. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. The detection was calibrated with polystyrene standards of narrow molecular weight distribution. The differential scanning calorimetric measurement (DSC) was performed with a TA instruments Q20 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10 $°C \cdot min^{-1}$ and a cooling rate of 10 °C min^{-1}. Glass transition temperature (T_g) was tested as the temperature of inflexion mid-point on heating. T_g was used to qualitatively estimate polymer chain flexibility.

Surface tension measurement. In this study, polymer-polymer interaction was qualitatively evaluated via surface tension measurements (Krüss DSA 100, pendant drop, at 25 °C) due to the approximately positive correlation of surface tension (γ) with cohesive energy density.[20,32]

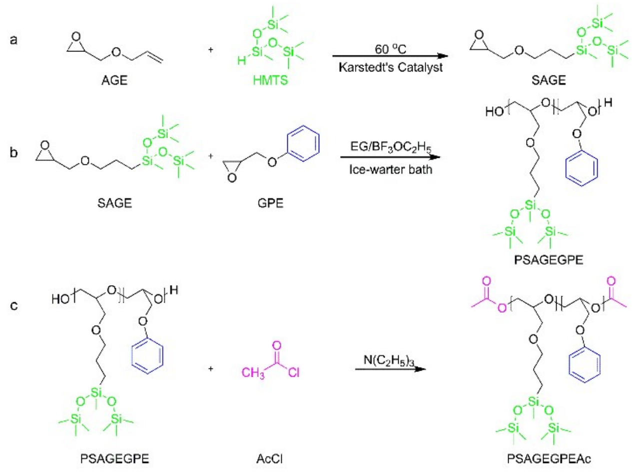
Solubility measurements in CO_2. The solubility was based on cloud point pressure (P_{cloud}) that higher cloud point pressure means lower solubility and that was performed in high pressure phase equilibrium apparatus as described before.[31,33] The process was repeated three times for each measurement. Typical deviations were approximately ± 0.5 MPa. All the measurements were conducted at 35 °C unless otherwise noted.

Viscosity measurements of polymer-thickened CO_2. The viscosity of polymer-thickened CO_2 was measured by Cambridge Viscosity's VISCOlab PVT (Pressure–Volume–Temperature) high-pressure viscometer (viscosity ranges: 0.02-10000 cp and accuracy: ± 1.0 %) with VISCOpro2000 system. The measurement setup is present in Fig. S1. The test was conducted at saturated solution condition at 35 °C. Slightly excess polymer sample was added into STIGMA Pump (Sanchez Technologies) and adjusting the pump to minimal volume for removing the air and then introducing CO_2 via a positive displacement pump. The temperature and pressure were adjusted at the desired value. The system was stirred vigorously for 1 h to promote dissolution of the polymer into CO_2 by mechanical agitation and the solution was allowed to stand for one hour before use to precipitate the undissolved polymer to the bottom of the pump. The solution was then introduced into PVT viscometer controlled at the same temperature for the viscosity test.

Synthesis of monomer. 1,1,1,3,5,5,5-Heptamethyl-3-(3-glycidyloxypropyl)- trisiloxane (SAGE) was synthesized by the hydrosilation reaction of AGE and HMTS catalyzed by Karstedt's Catalyst (Scheme 1a). 100 μL Karstedt's Catalyst were added into a mixture of 50 mL AGE and 138 mL HMTS at 60 °C and the reaction was stopped until its color turned yellow-brown from slightly yellow. The solution was diluted with chloroform and activated charcoal was added to remove the catalyst. Chloroform and unreacted reagents were removed by evaporation under reduced pressure, giving a colorless product (94 % yield) and characterized by ^1H NMR (400 MHz, $CDCl_3$) (see Fig. S2).

Synthesis of (co)polymers. The homopolymer PSAGE was prepared by the ring opening polymerization of SAGE. In a typical experiment, the mixture of 20 mL toluene, EG (1.24 g, 20.0 mmol) and Boron fluoride ethyl ether complex (0.52 mL) were stirred 30 min at room temperature, and then the solution of 25 mL (0.4 mol) of SAGE in 5 mL of toluene was added dropwise into the mixture over 1 h in an ice-water bath. The reaction was kept for 4 h and was terminated with aqueous $NaHCO_3$. The polymer solution was washed three times with pure water and the organic phase was dried with magnesium sulphate. The solvent and unreacted reagent was removed under vacuum at 80 °C. Yield =90 %.

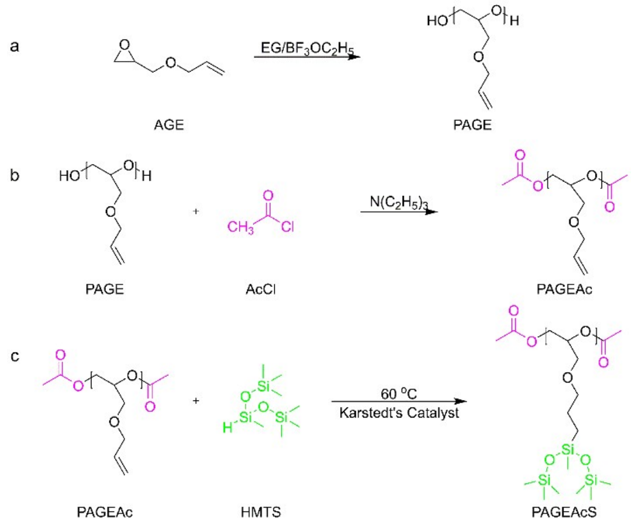
The copolymer 1,1,1,3,5,5,5-Heptamethyl-3-(3-glycidyloxypropyl)-trisiloxane-co-glycidyl phenyl ether (PSAGEGPE) was prepared by the copolymerization of SAGE and GPE with above similar procedure (Scheme 1b). Yield =91 %.



Scheme 1 Synthesis route of PSAGEGPEAc

Hydroxyl group can dramatically decrease the solubility of polymer in CO_2 due to the strong hydrogen bonding between hydroxyl groups, thus the CO_2-phobic hydroxyl group was modified to CO_2-philic acetate functional groups (Scheme 1c). Hydroxyl group of PSAGE and PSAGEGPE was capped through esterification reaction, marked as PSAGEAc and PSAGEGPEAc respectively, and the detail procedure was shown in Supporting Information.

Additionally, we also prepared HMTS modified polyether, marked as PAGEAcS, using post modification method via the hydrosilation reaction of HMTS with the carbon-carbon double bond side group of acetate groups capped poly(allyl glycidyl ether) (PAGEAc) (Scheme 2). The result was confirmed by ^{1}H NMR and GPC (Fig. S3 and S4).



Scheme 2 Synthesis route of PAGEAcS

3. Results and Discussion

3.1. Preparation and physical property of modified polyether

A series of HMTS modified polyether were synthesized via hydrosilation reaction, ring opening polymerization and esterification reaction. The results of molar mass and bulk composition were listed in Table 1. The content of GPE in copolymer was calculated according to the peak area of the hydrogen on methylene and methyne neighboring oxygen and that of phenyl group based on ^{1}H NMR (Fig. 1). End-capping was performed on these polymers and FTIR spectrum was taken to verify the completion of the esterification reaction (Fig. 2). As shown in Fig. 2, a strong absorption at 1745 cm^{-1} is observed after the esterification reaction which is according to the stretching vibration of carbonyl group in ester group. Simultaneously, the stretching vibration absorption peak of hydroxyl group at approximately 3500 m^{-1} thoroughly disappears, Thus the hydroxyl group was completely replaced by acetate.[28]

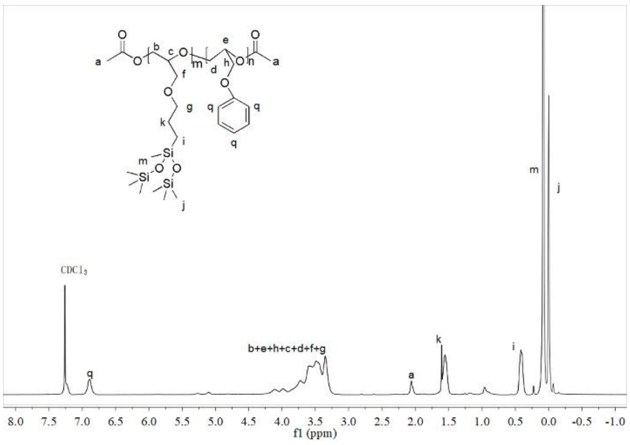


Fig. 1 ^{1}H NMR spectrum of PSAGEGPEAc

Surface tension and glass transition temperature were used to evaluate the polymer-polymer interaction and polymer chain flexibility, respectively. It can be seen from Table 1 that all the HMTS

Table 1 Physical Properties of prepared polymers

Run	Sample	Monomer feed ratio ($f_{SAGE} : f_{GPE}$)	M_n (g/mol)	M_w (g/mol)	PDI	Content of GPE (mol%)	T_g (°C)	$\gamma \pm 0.5$ (mN/m)
1	PAGEAc	-	1940	2510	1.30	0	-72	26.25
2	PAGEAcS	-	4200	5100	1.21	0	-75	19.58
3	PSAGEAc	-	2820	4130	1.46	0	-	-
4	PSAGEGPEAc-18.4%	8:2	3410	5030	1.47	18.4	-66	20.37
5	PSAGEGPEAc-27.8%	7:3	3340	5030	1.51	27.8	-63	20.42
6	PSAGEGPEAc-37.4%	6:4	3260	4630	1.42	37.4	-56	20.73
7	PSAGEGPEAc-48.1%	5:5	3050	4550	1.49	48.1	-51	21.59

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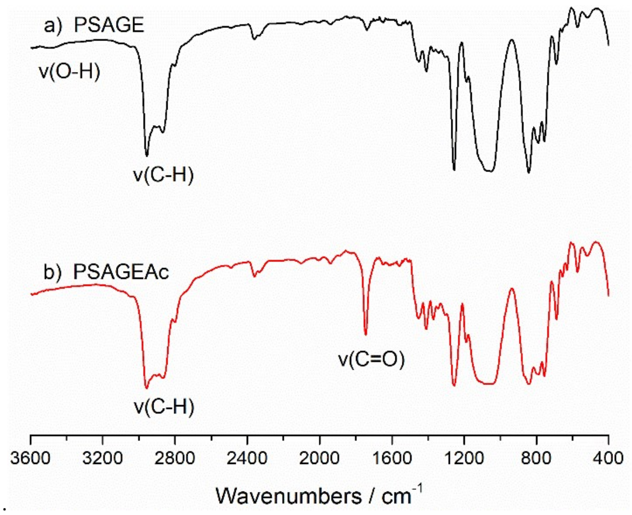

Fig. 2 FTIR spectra of PSAGE and PSAGEAc.

Modified polyethers (PAGEAcS, PSAGEAc and PSAGEGPEAc) show lower surface tension than PAGEAc. The surface tension value decreases from 26.25 mN/m for PAGEAc to about 20 mN/m for HMTS modified polyether, reveals that HMTS significantly weakens the polymer-polymer interaction. The T_g value of PAGEAcS drops about 2.8 °C compared with PAGEAc, which indicates HMTS also improves the chain flexibility of PAGEAc. However, the T_g values of these polymers rise up with an increase of GPE content, which is responsible for the reduced flexibility of these polymers.

3.2. Solubility of (co)polymers in CO_2

The solubility of PAGE, PAGEAc, PSAGEAc and PAGEACS in CO_2 was characterized with cloud point pressure measurements (See Fig. 3). We observed that PAGE was not miscible in CO_2 at pressure up to 35 MPa with the concentration as low as 0.2 wt %. However, the sample dissolved into CO_2 after the hydroxyl end groups was capped with acetoyl chloride, and the cloud point pressure of PAGEAc with M_n= 1940 g/mol was 24 MPa with concentration of 0.2 wt %. Obviously, the intermolecular interactions due to hydrogen bonding between hydroxyl group are dramatically decreased and the acetoxy group provide additional interaction with CO_2.[30] As expected, HMTS can further enhance the solubility of PAGEAc in CO_2. The cloud point pressures of HMTS modified product PAGEAcS with M_n= 4200 g/mol were 11.5-15.0 MPa with concentration range of 0.2-1.0 wt % and that of PSAGEAc with M_n= 2820 g/mol were 9-10 MPa with concentration range of 0.4-1.2 wt %. Weak polymer-polymer interaction and high chain flexibility are conductive for polymer dissolving in CO_2 due to the favorable enthalpy and entropy of mixing. We believe that HMTS improves the solubility of PAGEAc in CO_2 due to the weaker polymer-polymer interaction and higher chain flexibility as discussed above.

Fig. 4 shows that the experimental cloud point pressures of PSAGEGPEAc copolymer in CO_2 with concentration varying from 0.2 to 0.8 wt %. The copolymers become more difficult to dissolve in CO_2 as GPE content increased, because rigid phenyl groups decrease the polymer chain flexibility (higher T_g values, Table 1) and hence reduce the CO_2-phility of polymer (Fig. 5). Additionally, the π-π stacking interactions between phenyl groups are also detrimental to the dissolution of the polymer in CO_2.

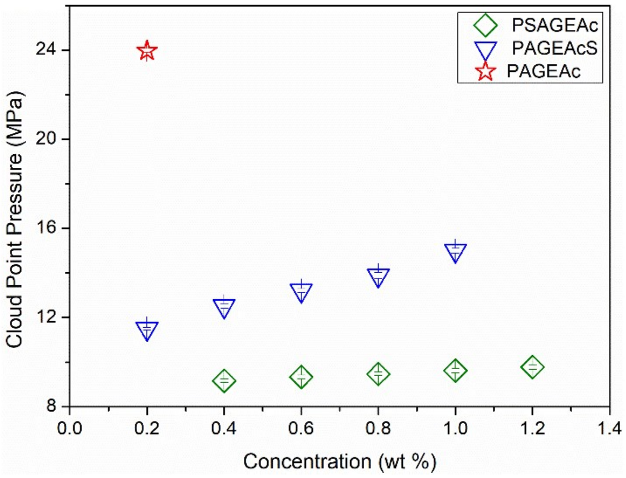

Fig. 3 Solubility of PAGEAc, PSAGEAc and PAGEAcS in CO_2.

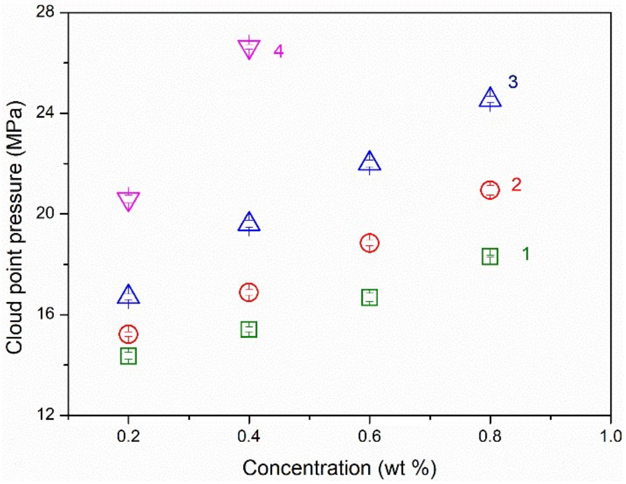

Fig. 4 Solubility of PSAGEGPEAc in CO_2: PSAGEGPEAc-18.4% (1), PSAGEGPEAc-28.5% (2), PSAGEGPEAc-37.4% (3) and PSAGEGPEAc-48.1% (4).

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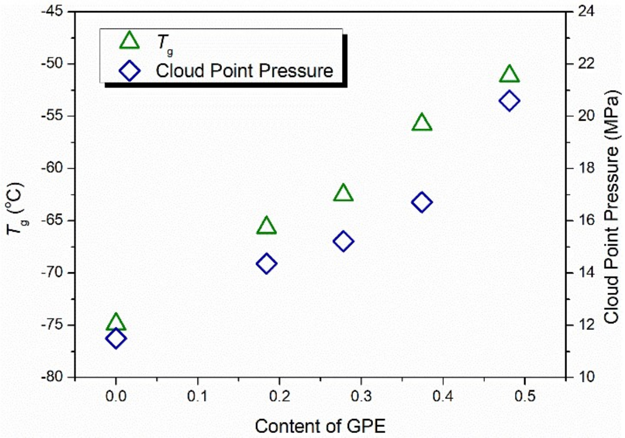

Fig. 5 Solubility and glass transition temperature values as a function of GPE molar percentage.

3.3. Evaluation of the viscosity of CO_2-polymer solution

It has been reported that Fluoroacrylate-styrene random copolymers with 1 wt % is able to thicken CO_2 about 3-10 fold by π-π interaction of phenyl group.[8] Here, we incorporated the phenyl group into HMTS modified polyether (PSAGEAc) via the copolymerization of SAGE and GPE, and the viscosity of CO_2-PSAGEGPEAc saturated solution was then evaluated at pressure range of 15-35 MPa, the result shown in Fig. 6. The viscosity of neat CO_2 was 0.07-0.11 cp at pressure range of 15-35 MPa at 35 °C, while the value of polymer thickened-CO_2 increased to 0.15-0.45 cp. All of the (co)polymers can increase the viscosity of neat CO_2 but at different degree according to the content of phenyl group. PSAGEAc, without phenyl group, can thicken CO_2 2.5-3.5 fold at pressure range of 15-30 MPa. Comparing to PSAGEAc, the copolymer PSAGEGPEAc-18.4%/CO_2 solution exhibits higher viscosity and the relative viscosity is up to 4-5 fold at pressure range of 15-35 MPa with less polymer concentration (exhibits relative low solubility than PSAGEAc). However, PSAGEGPEAc with higher phenyl group content (over 18.4 mol %) obtained less solution viscosity because of lower solubility (Fig. 7). These phenomena maybe explained by a synergistic combination of two factors. The bulky heptamethyltrisiloxane side groups along the polymer backbone are highly soluble in CO_2, yielding extended branches into CO_2. Intermolecular π-π interaction of phenyl group is another key factor to improve the viscosity of CO_2.[34,35] But the thickening effect decreases with excess phenyl group content as the phenyl group formed more intramolecular π-π stacking and less intermolecular π-π stacking, and also is detrimental for polymer dissolving into CO_2.[17,36]

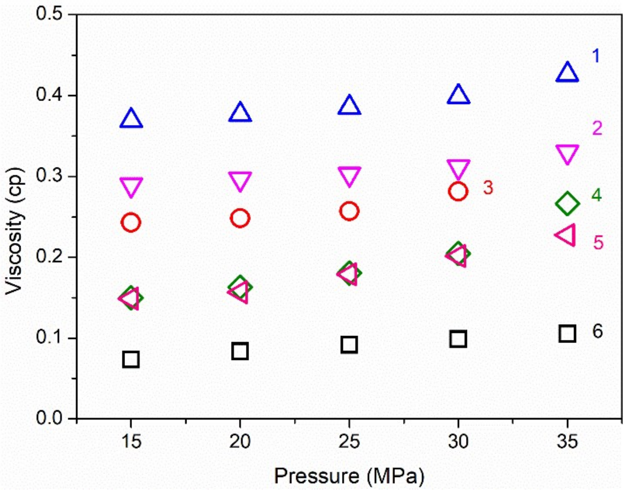

Fig. 6 Viscosity of pure CO_2 and polymer-CO_2 solution: PSAGEGPEAc-18.4% (1), PSAGEGPEAc-27.8% (2), PSAGEAc (3), PSAGEGPEAc-37.4% (4), PSAGEGPEAc-48.1% (5) and CO_2 (6).

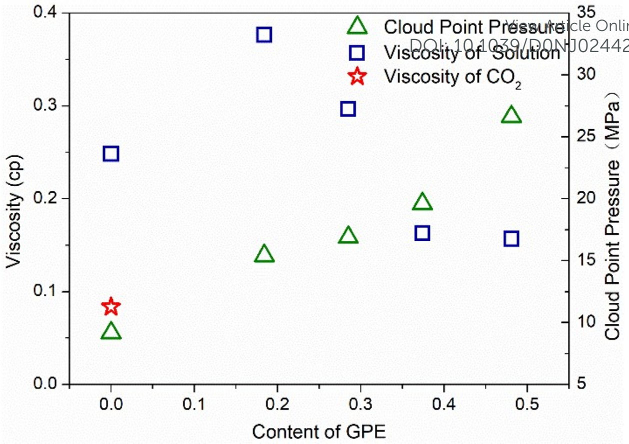

Fig. 7 Effect of GPE (content) on the viscosity of polymer-CO_2 solution at 20 MPa and the solubility of the polymer in CO_2 at a concentration of 0.4 wt %.

HMTS modified polyethers containing phenyl groups exhibit excellent CO_2 solubility and thickening ability stemmed from the successful molecular design strategy that the incorporation of CO_2-philic bulky silicon group and the CO_2-phobic aryl group respectively improve the CO_2 solubility and thickening ability of the polyether. Overall, the present work may propose a new perspective for the design of nonfluorous CO_2 thickeners.

4. Conclusions

A series of CO_2-soluble polyether thickeners were prepared via hydrosilation reaction, ring opening polymerization and esterification reaction. The solubility of PAGEAc in CO_2 was tremendous enhanced by modifying HMTS due to the decreased polymer-polymer interaction and improved chain flexibility. HMTS modified polyether (PSAGEAc) could effectively thicken CO_2, and incorporating moderate phenyl group into PSAGEAc can further enhance the thickening ability. PSAGEGPEAc with 18.4 mol % of phenyl groups exhibited the highest thickening capacity that increased the viscosity of CO_2 up to 4-5 fold at pressure range of 15-35 MPa in this work. However excessive phenyl contents are detrimental for the polymer dissolving in CO_2, thus reducing its thickening effect. This study would be conducive to the development of novel CO_2 thickener and provided a prospective platform for carbon dioxide enhanced oil recovery.

Conflicts of interest

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There are no conflicts to declare.

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Investigation on modified polyether as efficient CO_2 thickener

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Based on the CO_2-philic silicon group and the CO_2-phobic aryl group, silicon modified polyether exhibits both high solubility in carbon dioxide and high thickening ability to CO_2.

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