

Synthesis and physicochemical characterization of polyoxymethylene dimethyl ethers

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Abstract: Polyoxymethylene dimethyl ethers ($\text{H}_3\text{CO}(\text{CH}_2\text{O})_n\text{CH}_3$, PODE_n or DMM_n , $n \geq 2$) with unique physical and chemical properties are a potential additive for diesel fuels, which can effectively enhance the combustion efficiency and reduce the emission of pollutants. In this work, a series of pure PODE_n components ($n = 2-5$) were synthesized from methylal and trioxymethylene and obtained with high purity through collaborative separation; their structure and properties were characterized by NMR, FT-IR, Raman, DSC and DFT calculation and a detailed assignment of the expressions in the spectrogram to the various groups was performed. A detailed assignment of expressions in the spectrogram to the various groups was also performed. The density and viscosity of PODE_n were measured at 298.15–323.15 K. The results indicate that the density and viscosity of PODE_n decrease gradually with the increase of temperature. Meanwhile, with the increase in the number of $-\text{CH}_2\text{O}-$ units (n) from 2 to 5, the density, viscosity, flash point, pour point, and the heat of fusion and solidification of PODE_n are all increased with the increase in the chain length. These results are valuable for the practical synthesis and application of PODE_n .

Key words: polyoxymethylene dimethyl ethers; synthesis; structural characterization; physicochemical property

Polyoxymethylene dimethyl ethers ($\text{H}_3\text{CO}(\text{CH}_2\text{O})_n\text{CH}_3$, PODE_n or DMM_n , $n \geq 1$) are a series of polyether compounds with the smell of chloroform. They are similar in structure to methylal (viz., DMM or DMM_1) and can be obtained by inserting oxymethylene groups ($-\text{CH}_2\text{O}-$) into the methylal molecule^[1,2]. PODE_n are provided with some unique physicochemical properties such as low toxicity, excellent volatility, low condensation point, great permeating ability, good solubilizing power and miscibility with most organic compounds and water; the solubilities of PODE_2 and PODE_3 in water at 20°C are 30% and 28% by mass, respectively^[3,4]. PODE_n also exhibit high oxygen content (42%–51%) and cetane number (> 63)^[5]; as a promising diesel additive, they can improve the combustibility of diesel, enhance the efficiency of combustion and reduce the release of pollutants^[6-9]. To the best of our knowledge, PODE_n with n varying from 3 to 8 performed excellently as an oil additive, with very high cetane number (≥ 76), moderate boiling point, high flash point, and excellent miscibility with diesel oil. Such outstanding advantages give PODE_{3-8} higher efficiency in combustion and more convenience in storage and

transportation, in comparison with methylal which has a lower boiling point^[10]. Especially, the physicochemical properties of PODE_{3-8} matched well with that of diesel oil and could be blended directly into diesel without any change in the engine infrastructure^[11]; they have been considered as a potential diesel additive to further improve energy efficiency^[12]. Furthermore, PODE_n with good solubility could also be used as a substitute for some toxic organic compounds in industry and have received extensive attention in various applications.

The catalysts and processes used for the synthesis of PODE_n have been widely studied in the world; however, the physicochemical properties are rarely reported so far. It is necessary to accumulate enough data for chemical research and industrial application. In this work, therefore, a series of PODE_n components ($n = 2-5$) were synthesized from methylal and trioxymethylene and obtained with high purity through collaborative separation; their structure and properties were characterized by NMR, IR, Raman, DSC and DFT calculation. The basic physicochemical properties including density, viscosity, flash point, pour point and thermal properties of PODE_n monomers ($n = 2-5$) were then determined.

Received: 30-Mar-2017; Revised: 12-May-2017.

Foundation items: Supported by the National Natural Science Foundation of China (21473225).

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1 Experimental

1.1 Synthesis and separation of PODE_n

PODE_n were synthesized with methylal and trioxymethylene as the raw materials at 413.15 K and 2.0 MPa in N₂ for 2 h, with the functional ionic liquid as catalyst, as described in the literature^[13,14]. After reaction, PODE_n ($n = 1-8$) were produced, as listed in Figure 1; the ionic liquid was then separated from the reaction mixture by centrifugation and the mixed products of PODE_n ($n = 2-5$) were isolated by distillation.

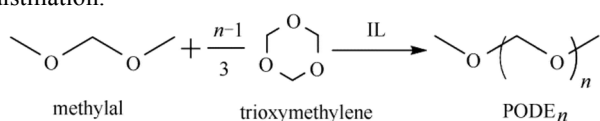


Fig. 1 Synthesis of PODE_n from methylal and trioxymethylene

To get the single component of PODE_n ($n = 2$ to 5), a rectifying column with 40 theoretical plates was used to separate the mixture. The single component compounds were identified by gas chromatography-mass spectrometry (GC-MS) (Agilent 7890A/5975C) and quantitatively analyzed by GC (Agilent 6890 equipped with a SE-54 capillary column). The mass fraction purities of the final PODE_n samples proved to be better than 0.999.

1.2 Physicochemical characterization of PODE_n

The ¹H and ¹³C NMR spectra in C₆D₆ were recorded on an Avance TM III-400MHz NMR spectrometer using tetramethylsilane (TMS) as an internal standard at the same time. The FT-IR spectra were recorded on a Nexus 870 infrared spectrometer with a resolution of 0.125 cm⁻¹ at room temperature, using the KBr pellet technique. The Raman spectra were collected at room temperature on an InVia Raman microscopic spectrometer with 1 cm⁻¹ resolution; the excitation source was a diode laser operating at 532 nm.

The molecular structure and the FT-IR and Raman spectra of PODE_n were speculated by density functional theory (DFT/B3LY) which can provide the vibration frequency^[15-17]. After the full optimization of the PODE_n molecular geometry, the theoretical calculation was then conducted under the conditions of room temperature and vacuum. The optimization of structure and energy was performed at the level of B3LYP/6-311+G (d, p) using Gaussian 09 software package; a scaling factor of 0.9613 was used for the calculation of vibration frequency^[18].

The density and viscosity of PODE_n ($n = 2, 3, 4, 5$) were determined on an Anton Paar Stabinger SVM3000 rotational automated viscometer at 293.15–323.15 K with an uncertainty of ±0.02 K. The equipment was calibrated with ethanol before

each measurement. The average of three measurements was reported; the overall accuracies of density and viscosity measurements at ambient pressure were better than ±5×10⁻⁴ g/cm³ and ±4%, respectively^[19].

The flash points were measured using a FP56 5G2 Tag closed-cup apparatus under (298±0.1) K and atmospheric pressure. The flash tester conformed to standards of ASTM D93, D1310, D3828, D3278, and D3941, as specified by the manufacturer. To ensure an acceptable precision, the dynamic flash point test method of D3941 was employed according to the physicochemical property of PODE_n, from which the deviation was determined.

The pour points of all samples were measured on a PAC-70X PHASE automatic analyzer that has a specified accuracy of ±0.1 K. The measurement was conducted according to ASTM D-5949 and the uncertainty of the pour point measurement complied with the testing standard.

Differential scanning calorimetry (DSC) was performed on a DSC200F3 TA instrument. The accuracy of temperature and enthalpy was ±0.1 K and ±0.1%, respectively, as specified by the manufacturer. The PODE_n samples were weighed inside hermetically sealed Al₂O₃ crucibles with a pinhole on the lid. The sample pan was placed in the calorimeter and subjected to the temperature programming in nitrogen, viz., cooling from room temperature to below the freezing point at 10 K/min, and then heating to above the melting point at 10 K/min.

2 Results and discussion

2.1 Characterization of PODE_n

From the ¹H NMR (400 MHz, BENZENE-D₆) and ¹³C NMR (100 MHz, BENZENE-D₆) spectra of PODE_n ($n = 2, 3, 4, 5$), following information was acquired: PODE₂, δ 3.11(s, 6H), 4.37(s, 4H), 55.07, 92.77; PODE₃, δ 3.12(s, 6H), 4.58(s, 4H), 4.78(s, 2H), 55.14, 87.86, 93.25; PODE₄, δ 3.11(s, 6H), 4.57(s, 4H), 4.78(s, 4H), 55.16, 88.35, 93.28; PODE₅, δ 3.10(s, 6H), 4.57(s, 4H), 4.80(s, 4H), 4.83(s, 2H), 55.26, 88.41, 88.87, 93.34. No impurity peaks are observed.

The FT-IR and Raman spectra of PODE_n ($n = 2, 3, 4, 5$) are shown in Figure 2 and Figure 3, respectively. All PODE_n are similar in the characteristics of spectrogram due to their analogous molecular structures. In the FT-IR and Raman spectra, the absorption peaks at 2950–2970 cm⁻¹ are attributed to asymmetric methyl (CH₃-) stretching vibrations, whereas the peaks around 2900–2960 cm⁻¹ to the asymmetric methylene (-CH₂-) stretching vibrations. The symmetrical methyl (CH₃-) and methylene (-CH₂-) stretching vibrations appear at 2820–2910 and 2780–2830 cm⁻¹, respectively^[20]. The deformation frequencies of methyl (CH₃-) and methylene (-CH₂-) are observed in the range of 1420–1480 and

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