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Mechanism of chain propagation for the synthesis of polyoxymethylene dimethyl ethers

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Abstract

Polyoxymethylene dimethyl ethers (PODE) were synthesized from the reaction of paraformaldehyde with dimethoxymethane (DMM) over different acid catalysts at different conditions. Products were found to follow the Schulz-Flory distribution law. The chain propagation proceeds through the insertion of an individual segment of CH_2O one by one, while the simultaneous insertion of a few CH_2O segments or their assembly is unlikely. Due to the restriction of this law, it is difficult to increase the selectivity to the desired products (e.g., $PODE_{3-4}$).

Key words

polyoxymethylene dimethyl ethers (PODE); diesel additive; chain propagation; product distribution; Schulz-Flory law

1. Introduction

By comparing to gasoline engine, diesel engine has the higher compression ratio and thermal efficiency and thus diesel is more economic than gasoline and produces less CO_x and NO_x [1]. Cetane number (CN) is an important index of diesel. With the consumption of petroleum, crude oils become heavier and the initial cetane numbers of diesel are usually low. Thus, the development of diesel additives with high oxygen contents and cetane numbers is highly desirable.

Polyoxymethylene dimethyl ethers (PODE) are a series of compounds with the formula $CH_3O(CH_2O)_nCH_3$, in which n is an integer equal to or greater than 1 (usually smaller than 8). These compounds are of high oxygen contents (42%–51%) and cetane numbers (>49) [2,3]. As diesel additives, they can improve the thermal efficiency by supporting burning of diesel in an engine, leading to the reduction of emissions of particular materials (PM), CO_x and NO_x. In addition, the boiling points and vapor pressures of PODE are in the range of diesel and thus they can be directly blended into diesel without the structural changes of diesel engines [4]. In fact, PODE have been considered as a potential diesel additive and suitable components are believed to be $PODE_{3-8}$, in which $PODE_{3-4}$ are more preferable [5].

PODE can be synthesized by the reaction of a compound (e.g, paraformaldehyde (PF), trioxane (TOX) or formaldehyde (FA)) providing the group of CH_2O as a chain segment with a compound (e.g., dimethoxymethane (DMM), dimethyl ether (DME) or methanol (MeOH)) providing methyl or methoxyl groups that can seal the ends of a chain. The reactions are catalyzed by acids [2,5−9]. Since all these reactants can be produced from methanol which is in turn produced from coal or biomass through syngas, the synthesis of PODE does not depend on the resources of petroleum. Thus, the use of PODE in diesel would reduce the dependency of world on petroleum. In fact, studies on the synthesis and application of PODE have received much attention worldwide [2,5−16]. However, little mechanistic studies on the reactions for the synthesis of PODE appeared in literature so far.

Schulz-Flory distribution theory was first developed to describe the distribution of masses of polymers with different chain lengths. Later, it was used to describe the mass distribution of hydrocarbons produced during the Fischer-Tropsch synthesis [17]. In this work, we studied the reactions for the synthesis of PODE and found that the products also followed the Schulz-Flory law.

2. Experimental

The reactions for the synthesis of PODE were carried out in a stainless steel autoclave lined with Teflon. In each run, 30.4 g DMM and 12 g PF were loaded into the 100 mL autoclave. The reactor was purged and sealed with N_2. The reactions were performed at the temperatures from 323 to 413 K for 2 to 48 h under magnetic stirring.

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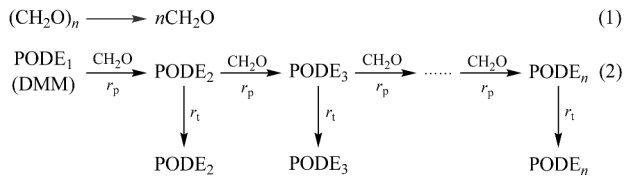
Sulfuric acid, an acidic carbon (prepared by the carbonization and sulfonation of a phenolic resin [18]) and a commercial acidic resin (D008) were used in this work for the synthesis of PODE. The surface areas of the solid catalysts were measured by the Gemini V 2380 autosorption analyzer and calculated by the Brunauer-Emmet-Teller (BET) method. Densities of surface acid sites of the solid catalysts were measured by the neutralization method as described in Ref. [18].

Reactants and products were analyzed by a gas chromatograph (GC) equipped with a SE-54 column connected to an FID for the detection of DMM, $PODE_n$, MeOH and TOX, and a Porapak-N column connected to a TCD for the detection of DMM, FA, MeOH and H_2O. The two data sets were correlated by the signals of DMM from the two detectors.

3. Results and discussion

The mechanism of chain propagation for the synthesis of PODE from DMM and PF can be described by Scheme 1, which showed the only forward reactions although the reversed reactions could not be denied. Thus, in this Scheme, r_p and r_t represent the net rates of chain propagation and termination, respectively. The chain propagation probability can be defined as $\alpha = r_p/(r_p+r_t)$. Apparently, larger is α, larger is the average molecular weight of PODE produced. According to Scheme 1, the probability for the formation of a $PODE_n$ with the chain length of n is α^n. Then, the number of CH_2O molecules of this $PODE_n$ should be equal to $N_n = C_1\alpha^n$ and the corresponding mass is $W_n = N_n nM = C_2 n\alpha^n$, in which C_1 and C_2 are proportion coefficients and M the molecular weight of CH_2O (a segment in the chain). By normalizing the masses of all PODE produced, i.e., by integrating W_n into 1 in $n =$ [0,], the coefficient C_2 can be solved and the equation $W_n = (\ln^2\alpha)n\alpha^n$ is obtained. This equation can be rewritten as a linear form $\ln(W_n/n) = n\ln(\alpha)+\ln(\ln^2\alpha)$, known as the Schulz-Flory equation. The linear relationship between $\ln(W_n/n)$ and n gives the slope $\ln(\alpha)$, from which the propagation probability factor (α) can be derived.



Scheme 1. Decomposition of paraformaldehyde and chain propagation for the synthesis of $PODE_n$

Table 1 gives the data for the synthesis of PODE from the reaction between DMM and PF at different temperatures using H_2SO_4 as a catalyst. $PODE_{2-7}$ were the main products. By plotting the data of masses of $PODE_{2-7}$ and that of unreacted DMM in Table 1 according to the Schulz-Flory equation, linear lines were obtained as shown in Figure 1. Thus, the PODE products produced by the reaction between DMM and PF follow the Schulz-Flory law. This clearly indicates that the chain propagation proceeds through the insertion of an individual segment of CH_2O one by one, and PF must be first decomposed into CH_2O. The simultaneous insertion of a few CH_2O segments or their assembly is unlikely. From the slopes of lines in Figure 1, the propagation probabilities were calculated to be 0.41, 0.40 and 0.38 for the synthesis of PODE from DMM and PF at temperatures of 373, 393 and 413 K, respectively. It seems that the propagation probability decreased a little with the increase of reaction temperature, which might be due to the effect of thermodynamic equilibrium. Since the reaction is exothermic, the equilibrium conversion of reactants decreases with the increase of reaction temperature [19]. Thus, the propagation probability might be correlated to equilibrium constants. Such correlation is important, but more data are needed to establish it. Since these propagation probabilities are small (0.38–0.41), the probability for the production of larger molecules of $PODE_n$ was low. Thus, the molecular weights of $PODE_n$ synthesized this way would be concentrated in a narrow range (n = 2–7), and the corresponding products might be used as diesel additives.

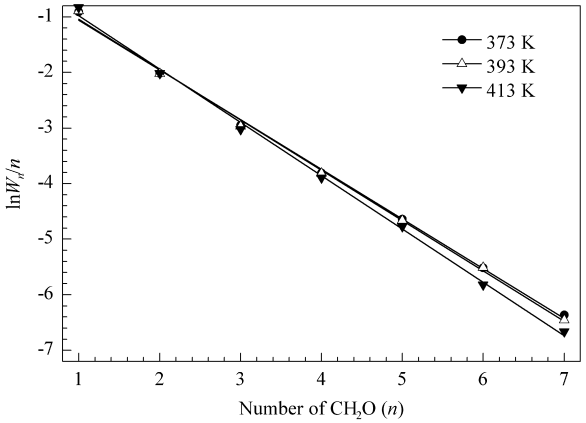


Figure 1. Schulz-Flory distribution of $PODE_n$ synthesized from the reaction between dimethoxymethane and paraformaldehyde at different temperatures (see Table 1)

Table 1. Synthesis of PODE from the reaction between DMM and PF (DMM = 30.4 g, PF = 12.0 g, H_2SO_4 = 0.05 g and t = 2 h)

Reaction temp. (K)	DMM conv. (%)	PF conv. (%)	Product distribution (wt%)										Propagation probability (α)	Selectivity to $PODE_{2-7}$	Selectivity to $PODE_{3-4}$
			$PODE_1$ (unconverted)	$PODE_2$	$PODE_3$	$PODE_4$	$PODE_5$	$PODE_6$	$PODE_7$	FA	MeOH	TOX			
373	48.7	79.5	36.8	24.3	14.3	8.1	4.4	2.2	1.1	5.8	2.7	0.3	0.41	54.4	22.4
393	48.0	78.8	37.3	24.1	14.0	8.0	4.3	2.2	1.0	6.0	2.8	0.3	0.40	53.6	22.0
413	45.2	77.0	39.3	23.9	13.1	7.3	3.8	1.6	0.8	6.5	3.3	0.4	0.38	50.5	20.4

Note: Selectivity of products is defined as the weight of products divided by the total mass of reactants charged into the reactor

The adaptability of Schulz-Flory law for the synthesis of PODE was studied using different reactants and catalysts at different reaction conditions. Table 2 shows the results.

The acidic carbon used in this work possessed the surface area of about 56 $m^2 \cdot g^{-1}$, total acid sites of about 5 $mmol \cdot g^{-1}$ and strong acid sites (–SO_3H) of about 1.5 $mmol \cdot g^{-1}$. The commercial acidic resin (D008) contained the sulfonated groups of about 3.2 $mmol \cdot g^{-1}$.

Plotting the data in Table 2 according to the Schulz-Flory equation obtained the linear lines shown in Figure 2. Thus, the $PODE_n$ synthesized with different reactants and catalysts at different conditions follow the Schulz-Flory law. In particular, the two solid catalysts were effective for the synthesis of $PODE_n$, and the development of solid acid catalysts is desirable since the reactions would be more environmentally benign.

Table 2. Synthesis of PODE from different reactants at different reaction conditions

Reactants	Catalyst	BET area ($m^2 \cdot g^{-1}$)	Mass (g)	Number of protons (mmol)	Reaction conditions	Product distribution (wt%)							Propagation probability (α)
						$PODE_1$	$PODE_2$	$PODE_3$	$PODE_4$	$PODE_5$	$PODE_6$	$PODE_7$	
DMM+TOX	Acidic carbon (sulfonated)	56	0.5	0.75	323 K, 48 h	36	25.6	15.4	8.8	3.9	2.6	1.2	0.41
DMM+PF	Acidic resin D008	N/A	0.5	1.6	393 K, 2 h	38.7	24.8	13.5	6.7	2.9	1.2	0.4	0.34
$PODE_2$	H_2SO_4	N/A	0.05	1.02	393 K, 2 h	39.5	26.8	14.6	6.6	2.1	0.6	0	0.31

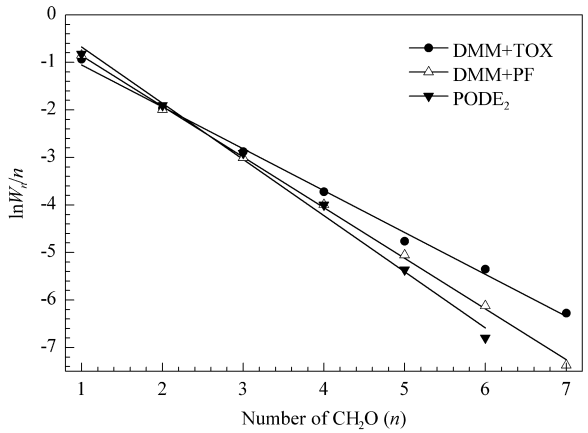


Figure 2. Schulz-Flory distribution of $PODE_n$ synthesized from different reactants using different catalysts at different reaction conditions (see Table 2)

When trioxane was used as a reactant with DMM, the products still follow the Schulz-Flory law, indicating that it was also first decomposed into CH_2O. No $PODE_4$ was produced by the direct insertion of trioxane.

$PODE_2$ was also used as a reactant (see Table 2), which can be taken as a complex of DMM and CH_2O with the ratio of CH_2O/DMM = 1. When 30.4 g DMM and 12 g PF were used (see Table 1) for the synthesis of PODE, the ratio of CH_2O/DMM was 1, same as that in $PODE_2$. It is interesting to note that as catalyzed by sulfuric acid, $PODE_2$ was decomposed and DMM and $PODE_{n>2}$ were produced. The products (including unconverted $PODE_2$) follow the Schulz-Flory law. Thus, the synthesis of $PODE_n$ from $PODE_2$ alone follows the same chain propagation mechanism as that from the reaction of PF with DMM. More specifically, the chain propagation mechanism must involve the following three steps: (1) PF or TOX is decomposed into the CH_2O segments while DMM may be decomposed into CH_3OCH_2O– + –CH_3 or CH_3O– + –CH_2OCH_3. (2) CH_2O segments are added one by one onto CH_3OCH_2O– or –CH_2OCH_3 with the net rate of r_p. (3) The chain is terminated by the addition of a methyl or methoxyl group onto the end with the net rate of r_t for the formation of a $PODE_n$ with the chain length of n. However, the propagation probability for the synthesis of $PODE_n$ from $PODE_2$ was a little bit lower ($\alpha = 0.31$). This seems to indicate that the rate of chain propagation might be affected by the rate of decomposition of a reactant. Right now, this effect is not clearly understood. The ratio of rates for the chain propagation and termination can be derived from the propagation probability α. The ratio of r_t/r_p equals to 2.3 and 1.5 when α equals to 0.3 and 0.4, respectively. Thus, the rate of chain termination is faster than that of propagation during the synthesis of PODE.

4. Conclusions

In summary, DMM ($PODE_1$) would be always the most abundant in the products, no matter what kind of reactants and reaction conditions are used for the synthesis of PODE since the propagation probabilities are low (as compared to those for polymers and Fischer-Tropsche synthesis) according to the Schulz-Flory law. To increase the selectivity to a specific product $PODE_n$ is unlikely, since the quantities of all the products of PODE are correlated by the law. Thus, the separation of desired products (e.g., $PODE_{3-4}$) is extremely important and other products and by-products must be separated and recycled.

Acknowledgements

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