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Factors Inhibiting the Alkyl-Branch Plasticization of Polyoxymethylene

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Summary: The ability of an alkyl branch to depress the melting temperature in a polyoxymethylene chain is measurably less than that in a polyethylene chain. The factors that inhibit the alkyl-branch plasticization of polyoxymethylene are considered by computational assessment of a series of model compounds at various levels of theory: DFT B3LYP 6-31+G*, DFT B3LYP 6-311++G**, MP2 cc-pVTZ, T1, and G3(MP2). Intramolecular interactions—characterized as acetal CH···O hydrogen bonds—are surprisingly strong and likely encourage conformational regularity in the vicinity of the alkyl branches, allowing maintenance of the intermolecular chain-chain interactions. The acetal CH···O hydrogen bonds in dimethylene glycol average to 2.65 kcal/mol while the non-acetal CH···O interactions in 1,3-propanediol are much weaker with an average of 0.34 kcal/mol (G3(MP2)). The related, classical OH···O hydrogen bond in ethylene glycol is found to be worth 2.12 kcal/mol. To describe this energetic ordering, an additional stabilizing anomeric effect is invoked for dimethylene glycol, a model for polyoxymethylene.

Keywords: branching; hydrogen bonding; molecular modeling; polyoxymethylene; renewable resources

Introduction

The lifecycle of polyoxymethylene (POM, also called polyformaldehyde or acetal polymer) is shown in Figure 1. The dominant commercial route to methanol is from natural gas via synthesis gas (carbon monoxide + hydrogen). From methanol, 7.5 billion kg of formaldehyde are produced each year,[1] of which about 500 million kg are devoted to the synthesis of polyoxymethylene via two main routes.[2] The first route employs anionic polymerization of formaldehyde to form POM, which is then capped with acetic anhydride to prevent thermal depolymerization. The second route relies on the ring-opening polymerization of trioxane, the cyclic trimer of formaldehyde. This is copolymerized with 1,4-dioxane or ethylene oxide to provide polyether linkages that are not readily susceptible to thermal depolymerization. POM is an engineering plastic that is used routinely in engine parts, appliances, plumbing and hardware, electronic components, zippers, and machinery.

Feedstocks for Polyoxymethylene

As described in Figure 1, an alternative source of methanol is wood via its destructive distillation (pyrolysis) to provide "wood alcohol." Current technology is calculated to produce up to 59 kg of methanol from 100 kg of wood.[3] While the preparation of methanol from cellulose is no longer extensively practiced, this process will almost certainly be of great interest again in the future if the cost of natural gas increases or supply channels are disrupted.[4] Importantly, the monomer formaldehyde can be derived either from natural gas or from biomass.

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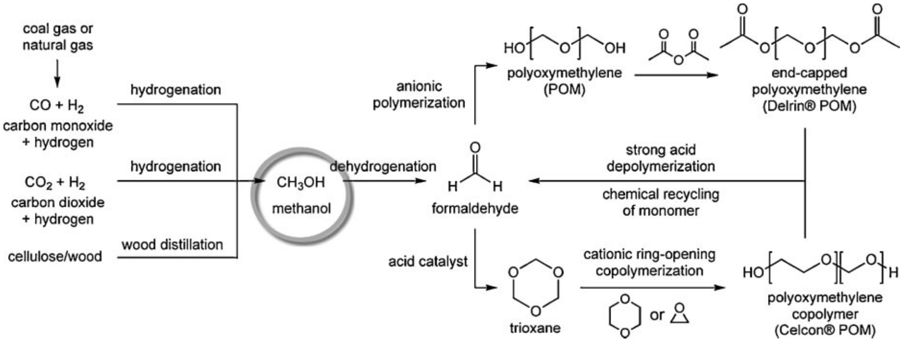


Figure 1.
The chemical lifecycle of polyoxymethylene (POM). Note that this polymer can originate from a variety of feedstocks and can be chemically recycled to afford the original formaldehyde monomer.

While polylactic acid (PLA) is probably the most successful thermoplastic made from biorenewable feedstocks, it derives from starch, which is considerably less abundant than cellulose. Moreover, diverting our starch resources to chemical and polymer production directly impacts the food supply. Utilization of cellulose, the most abundant polymer in the biosphere, avoids this food supply issue and its conversion to formaldehyde or trioxane avoids the problems associated with cellulose digestion and sugar fermentation.

Branched Polyoxymethylene

The mechanical properties of high density polyethylene (HDPE) are markedly perturbed by copolymerizing ethylene with small amounts of α-olefins—typically 7% by weight, which is about 2 mol% 1-octene incorporation.[5] Compared to HDPE, linear low density polyethylene (LLDPE) exhibits a decreased T_m, a lower tensile modulus and tensile strength, but a much improved impact strength. These effects are normally interpreted on the molecular scale as a local disruption of the crystalline lattice by the introduction of an alkyl branch. The incorporation of branches into POM to form linear low density polyoxymethylene (LLDPOM) should have a similar plasticizing effect, widely expand the properties of POM, and allow for precise control over the polymeric properties.

Somewhat surprisingly, investigations of branched polyoxymethylene are rare and had been conducted only to address the thermal depolymerization tendencies of POM, not for the purpose of tuning the melting temperature and other thermomechanical properties.[6–8] A useful comparison to commercial LLDPE resins, having 1 to 25 mol% comonomer incorporation,[5] was not possible until our recent report.[9] Our approach for incorporating well-defined branches into otherwise linear polyoxymethylene exploited the cationic ring-opening copolymerization of trioxane and either 1-alkene oxides or 4-alkyl dioxolanes (Figure 2).[9]

As predicted, the melting temperatures of the LLDPOM copolymers are depressed compared to that of POM homopolymer

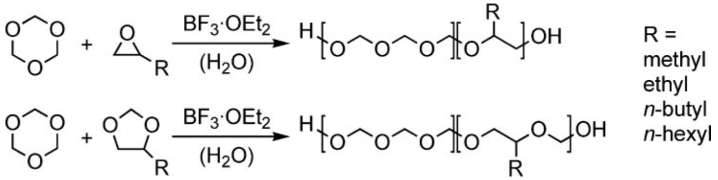


Figure 2.
Copolymerization strategies for LLDPOM: trioxane with alkene oxides or 4-alkyl dioxolanes.

($T_m = 181\,°C$). Figure 3 illustrates the dependence of copolymer melting temperature on branch density (BD)—here quantified as the number of branches per 1000 main chain atoms. Note that the melting temperature is linearly correlated to the branch density, but is ostensibly independent of the comonomer's identity (epoxide or dioxolane; R = methyl, ethyl, *n*-butyl, or *n*-hexyl).

LLDPOM versus LLDPE

Regression analysis for 43 LLDPOM copolymers yields the linear relationship $T_m = 170.9 - 0.45(BD)$ (Figure 3).[9] A related analysis by Mirabella and Crist[10] for a series of LLDPE copolymers yields $T_m = 131.4 – 1.17(BD)$. The calculated slopes directly measure an alkyl branch's ability to disrupt crystallinity. For LLDPE a 10 °C melting point depression is effected with 8.5 branches per 1000 main chain atoms; in contrast, the same melting point depression in LLDPOM requires 22 such branches. The quotient of the slopes in Figure 3 provides the first and only quantitative ''branch effect'' comparison between these two polymer classes. Approximately 2.6 times more branches ($= -1.17/-0.45$) are required to plasticize polyoxymethylene than polyethylene. Most likely, a branch is less effective for LLDPOM (slope = −0.45) because its numerous local dipoles result in stronger intermolecular chain–chain interactions than those present in the hydrocarbon polymer (slope = −1.17).

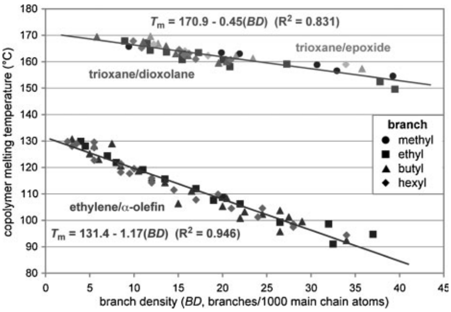


Figure 3.
Comparative melting point trends for polyoxymethylene copolymers[9] (top) and polyethylene copolymers[10] (bottom) as a function of branch density.

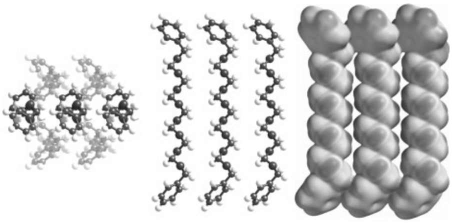


Figure 4.
Intermolecular chain-chain interactions are weak in this lattice plane. The electrostatic potential energy map indicates minimal electron density between the chains (DFT B3LYP 6-31G*).

Intermolecular Chain–Chain Interactions

An important model for the polyoxymethylene chain can be found in 1,17-diphenyl-2,4,6,8,10,12,14,16-octaoxaheptadecane ($Ph(CH_2O)_8CH_2Ph$), which contains eight oxymethylene units and has been structurally characterized by X-ray crystallography.[11] We have analyzed the packing structure of this compound in search of intermolecular chain-chain interactions. In the lattice plane depicted in Figure 4, it appears that the chains are not oriented properly to interact the δ^+ of the acetal hydrogens with the δ^- of the oxygens. The electrostatic potential map reveals minimal electron density between the chains (Figure 4). We sought a means to measure the strength of the intermolecular chain-chain interactions and decided on the model compounds depicted in Figure 5, dimethoxymethane and dimethyl ether. These are spliced directly from two adjacent polymer chains in the lattice structure

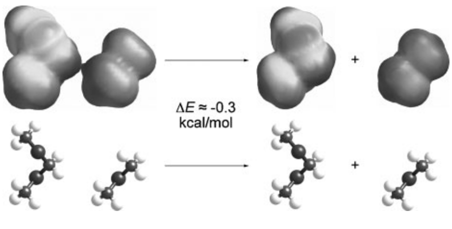


Figure 5.
Model compounds indicate a weakly repulsive H···H interaction between adjacent polymer chains. Their separation is favored by about 0.3 kcal/mol (DFT B3LYP 6-31G*, DFT B3LYP 6-311++G**).

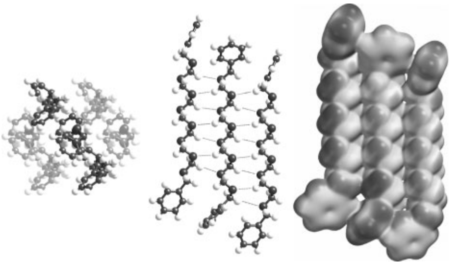


Figure 6.
Intermolecular chain-chain interactions are prominent in this lattice plane. The electrostatic potential energy map indicates significant electron density between the chains (DFT B3LYP 6-31G*).

and aptly approximate a localized H···H interaction between the chains. However, the interaction energy is calculated to be slightly repulsive: -0.32 kcal/mol (DFT B3LYP 6-31G*); and -0.36 kcal/mol (DFT B3LYP 6-311++G**).[12]

Consider now the lattice plane depicted in Figure 6. These chains, indeed, appear to have significant interaction between the δ^{+} of the acetal hydrogens and the δ^{-} of the oxygens. The electrostatic potential map reveals significant electron density between the chains (Figure 6). Computational analysis of appropriately aligned model compounds—spliced directly from the lattice structure—indicates that the CH···O interaction is attractive and therefore stronger than the H···H interaction energy calculated by modeling the other lattice plane: +0.98 kcal/mol (DFT B3LYP 6-31G*); +0.20 kcal/mol (DFT B3LYP 6-311++G**).

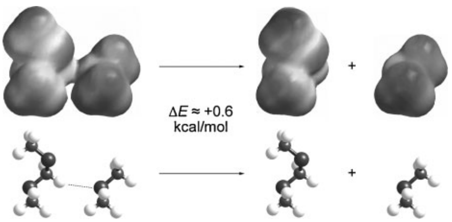


Figure 7.
Model compounds indicate an attractive CH···O interaction between adjacent polymer chains. Their separation is disfavored by an average of 0.6 kcal/mol (DFT B3LYP 6-31G*, DFT B3LYP 6-311++G**).

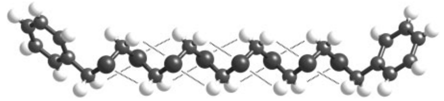


Figure 8.
Intramolecular 1,5 H···O interactions in a polyoxymethylene model[11] denoted by the dashed lines. The fourteen internuclear distances (from left to right) are: 2.535, 2.557, 2.564, 2.575, 2.552, 2.564, 2.559, 2.559, 2.564, 2.552, 2.575, 2.564, 2.557, and 2.535 Å.

Intramolecular Chain–Chain Interactions

In addition to the intermolecular chain-chain interactions that exist between polyoxymethylene chains, there appear to be related CH···O interactions within a given chain. It is known that POM typically adopts an all

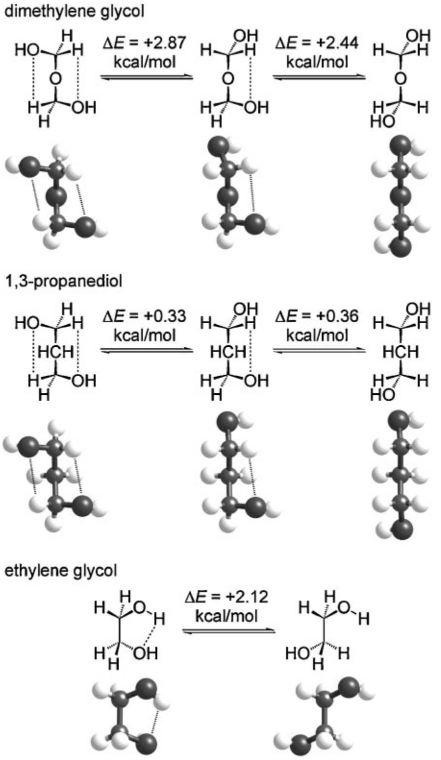
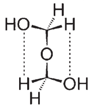
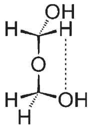
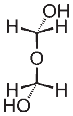
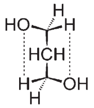
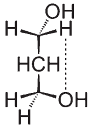
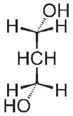
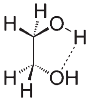
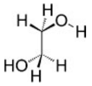


Figure 9.
Energy costs for disrupting H···O interactions, computed according to the G3(MP2) algorithm. The internuclear H···O distances are: 2.548, 2.548, and 2.692 Å, respectively for dimethylene glycol; 2.610, 2.609, and 2.646 Å, respectively for 1,3-propanediol; and 2.224 Å for ethylene glycol.

(approximately) *gauche* helix[13] and this allows the relatively close 1,5 H···O interactions denoted by the dashed lines shown for 1,17-diphenyl-2,4,6,8,10,12,14,16-octaoxaheptadecane in Figure 8.

In order to model this intramolecular CH···O interaction, the surrogate compound dimethylene glycol has been studied computationally with various levels of theory. Depending on the conformation of dimethylene glycol there can be two, one, or zero CH···O interactions, as depicted in Figure 9. Thus, the ground state energy differences among these conformers provide a measure of the strength of the acetal CH···O hydrogen bond. According to the G3(MP2) method, these interactions are worth 2.87 and 2.44 kcal/mol. Table 1

Table 1.
Relative energies (in kcal/mol) of dimethylene glycol, 1,3-propanediol, and ethylene glycol as a function of conformation. The energies include the zero-point energy correction.

Model	Method				
	DFT B3LYP 6-31+G*	DFT B3LYP 6-311++G**	MP2 cc-pVTZ	T1	G3(MP2)
dimethylene glycol					
	0.000	0.000	0.000	0.000	0.000
	2.500	2.442	2.831	3.241	2.868
	4.792 ($\Delta = 2.293$)	4.599 ($\Delta = 2.156$)	5.298 ($\Delta = 2.467$)	5.961 ($\Delta = 2.720$)	5.305 ($\Delta = 2.437$)
1,3-propanediol					
	0.000	0.000	0.000	0.000	0.000
	0.380	0.077	0.452	0.468	0.332
	0.648 ($\Delta = 0.267$)	0.169 ($\Delta = 0.092$)	0.983 ($\Delta = 0.531$)	0.975 ($\Delta = 0.507$)	0.687 ($\Delta = 0.355$)
ethylene glycol					
	0.000	0.000	0.000	0.000	0.000
	2.432	2.089	2.195	2.323	2.121

reports that similar numbers were found for other levels of theory.

For comparison, a non-acetal model compound was investigated. Depending on its conformation, 1,3-propanediol can also have two, one, or zero CH···O interactions; however, these involve non-acetal hydrogens and therefore the δ^+ on H should be less than that in dimethylene glycol. Indeed, the penalty for disrupting the CH···O interactions in 1,3-propanediol is comparatively meager and ranges from about 0.1 to 0.5 kcal/mol (Table 1).

A final model for comparison is ethylene glycol, which can attain an intramolecular, classical OH···O hydrogen bond.[14] The strength of this hydrogen bond is calculated to be 2.1 kcal/mol according to G3(MP2) and consistently lower than the CH···O interaction in dimethylene glycol, regardless of the computational method (Table 1). One explanation for this energetic ordering is the added anomeric stabilization[15] found in the dimethylene glycol conformers which is lost at the same time that the CH···O interaction is lost via conformational motion. This anomeric stabilization effect is absent in the other model compounds, 1,3-propanediol and ethylene glycol.

Conclusions

Our previous investigations of alkyl-branched polyoxymethylenes revealed that considerably more branches are required to plasticize polyoxymethylene than polyethylene.[9] About 2.6 times more branches are required to effect a comparable melting point depression in POM versus PE. The present computational model studies help to explain the diminished response of POM to chain disruptions. The numerous local dipoles of POM lock adjacent helical chains together. In particular, intermolecular CH···O interactions are abundant and strong. Within a chain, the observed helical conformation has two reinforcing effects: intramolecular 1,5 H···O interactions and anomeric stabilization. The penalty for disrupting these (simultaneously) is calculated to be 2.2 to 3.2 kcal/mol, depending on the computational method. When non-acetal hydrogens are involved, the penalty for disrupting a 1,5 H···O interaction is considerably less: 0.1 to 0.5 kcal/mol. For comparison, a classical 1,5 H···O hydrogen bond is calculated to be about 2.1 to 2.4 kcal/mol, consistently less than the 2.2 to 3.2 kcal/mol values computed for the polyoxymethylene analogue. The strong inter- and intramolecular forces suggest that significantly plasticized polyoxymethylene copolymers will require rather high comonomer compositions. For this and other reasons we continue our pursuit of more effective and economical approaches to polyoxymethylene plasticization.

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[1] K. Weissermel, H.-J. Arpe, "*Industrial Organic Chemistry*", Wiley-VCH, Weinheim **2003**, p. 38.

[2] G. Odian, "*Principles of Polymerization, Fourth Edition*", Wiley-Interscience, New York **2004**, p. 448.

[3] D. J. Moorhead, "Researchers Say Methanol From Trees Could Revitalize Rural Economies", *The Forestry Source*, March **2005**.

[4] [4a] J. I. Zerbe,*World Resource Review* **1987**, 3(4), 406–414; [4b] J. M. Norbeck, K. C. Johnson, "Evaluation of a Process to Convert Biomass to Methanol Fuel" Final Report to U.S. Environmental Protection Agency under Cooperative Agreement CR824308-01-0. NRMRL-RTP-202 2R9/28/00, **2000**; [4c] W. P. M. van Swaaij, S. R. A. Kersten, F. G. van den Aarsen, "Routes for methanol from biomass" Conference on Sustainable Industrial Developments, Delfzijl, The Netherlands, April **2004**.

[5] D. M. Simpson, G. A. Vaughan, "*Encyclopedia of Polymer Science and Technology, Vol. 2*", H. F. Mark, Ed., John Wiley & Sons, New York **2003**, pp. 441–482.

[6] Asahi Chemical Industry Co., Ltd., Japan "Polyoxymethylene molding compositions" *Japanese Patent* 59129247, **1984**.

[7] [7a] Celanese Corp. of America "Poly(oxymethylenes) and poly(oxyalkylenes)" *Belgian Patent* 619654, **1962**. [7b] S. Yahiro, T. Hata, K. Matsuzaki, "Preparation

of biodegradable polyoxymethylenes'' *Japanese Patent* 04108819, **1992**. [7c] T. Murao, K. Yamamoto, G. Reuschel, D. Fleischer, ''Blow or extrusion molding product of polyoxymethylene resin and process for producing the same'' *European Patent* 568308, **1993**.

[8] D. Braun, U. Bruckner, P. Eckardt, M. Hoffmockel,*Angew. Makromol. Chem.* **1999**, *265*, 55–61.

[9] A. D. Ilg, C. J. Price, S. A. Miller, *Macromolecules* **2007**, *40*, 7739–7741.

[10] F. M. Mirabella, B. Crist, *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 3416–3427.

[11] J. W. Bats, C. Miculka, C. R. Noe, *Acta Cryst.* **2007**, *C63*, o190–o192.

[12] All computational studies were performed with Spartan '06 for Macintosh, version 1.0.3 software package. The reported energies include the zero-point energy correction.

[13] R. A. Sorensen, W. B. Liau, L. Kesner, R. H. Boyd, *Macromolecules* **1988**, *21*, 200–208.

[14] [14a] V. Viti, P. L. Indovina, F. Podo, L. Radics, G. Némethy,*Mol. Phys.* **1974**, *27*(2), 541–549. [14b] P. I. Nagy, W. J. Dunn, III, G. Alagona, C. Ghio, *J. Am. Chem. Soc.* **1992**, *114*, 4752–4758.

[15] [15a] I. Tvaroska, T. Bleha, *Can. J. Chem.* **1979**, *57*, 424–435. [15b] A. Karpfen, A. Beyer, *J. Comput. Chem.* **2004**, *5*, 19–23.