

京都大学教育研究振興財団助成事業  
成 果 報 告 書

2022 年 5 月 2 日

公益財団法人京都大学教育研究振興財団

会 長 藤 洋 作 様

所 属 部 局 工学研究科・高分子化学専攻・先端機能高分子講座C

職 名 講師

氏 名 ランデンバーガー キラ ベス

助 成 の 種 類	令和 3 年 度 ・ 研究活動推進助成			
申請時の科研費 研究 課 題 名	新しい分子間相互によるポリマー構造および性質の影響の検討			
上記以外で助成金 を 充 当 した 研 究 内 容	なし			
助成金充当に関 わる共同研究者	(所属・職名・氏名) 京都大学大学院工学研究科・修士課程・隆永鈴木 および 西村希望 京都大学大工学研究科・学部・栃谷魁斗			
発表学会文献等	(この研究成果を発表した学会・文献等) 第70回高分子討論会「ハロゲン結合可能なビニルエーテルモノマーによるポリマー合成及びその解析～自己組織化を目指して～」、2021/9/7 鈴木隆永、オンライン ACS Spring 2022「Investigation of the influence of polymer structure on the halogen bonding ability of novel poly(vinyl ether)s containing perfluoriodobenzene moieties」、2022/3/22、鈴木隆永、栃谷魁斗、ランデンバーガー キラベス、オンライン			
成 果 の 概 要	研究内容・研究成果・今後の見通しなどについて、簡略に、A4版・和文で作成し、添付して下さい。(タイトルは「成果の概要／報告者名」)			
会 計 報 告	交付を受けた助成金額	1,000,000	円	
	使用した助成金額	1,000,000	円	
	返納すべき助成金額	0	円	
	助成金の使途内訳	費 目	金 額	
		化合物および実験用消耗品	304,689	
		実験用のガラス器具	213,675	
		国際学会参加費	23,371	
		ロータリーエバポレータ	146,960	
純水器		138,330		
冷却水循環装置	172,975			
当財団の助成につ いて	(今回の助成に対する感想、今後の助成に望むこと等お書き下さい。助成事業の参考にさせていただきます。) 支援があるために研究が続きましたので感謝しています。			

## 成果の概要/ランデンベーカー キラ ベス

### 研究内容

This research aims to develop novel self-assembling polymers using halogen bonding interactions and poly(vinyl ether)s as a means to investigate the effects of polymer backbones on self-assembly properties, with the purpose of forming better supramolecular polymer networks (SPN). Halogen bonding is the intermolecular interaction between the electron-poor  $\sigma$ -hole on a halogen (I, Br or Cl) and an electron-rich Lewis base (often O or N), and while potentially as strong as hydrogen bonding, it is, comparatively, underrepresented. For polymer self-assembly materials, poly(vinyl ether)s, with a more flexible backbone than most other polymers, are also underrepresented. SPN are network structures of polymers held together by directional and specific non-covalent interactions at netpoints and have great potential as self-healing materials.

The research supported by this grant enabled steps towards the formation of SPN and consisted of three main research focuses: 1) synthesis of polymer structures using novel halogen bonding vinyl ether monomers that were previously developed in our lab, 2) development of halogen bond acceptors, and 3) investigation of the halogen bonding ability of the formed materials and any self-assembly structures.

### 研究成果

A variety of polymer structures were successfully synthesized using the novel halogen bonding vinyl ether monomers developed in our lab and included AB block copolymers and random copolymers. Initial investigations were also made into the synthesis of ABA triblock copolymers, but these studies are still ongoing. Copolymers were created using isobutyl vinyl ether (IBVE) as the comonomer, as this should not participate in halogen bonding. For the samples created a 1:2 ratio of halogen bonding vinyl ether monomer to IBVE was synthesized. Controlled polymerization was achieved for all samples.

Synthesis of star-shaped polymers was also investigated. Star-shaped polymers offer increased contact points and are expected to ease the formation of SPN. An extensive study into determining amenable conditions for the formation of star-shaped polymers using these novel vinyl ether monomers was carried out. All three halogen bonding monomers allowed for the formation of well-developed star-shaped polymers, but ratio of crosslinker varied with the type of monomer.

Various attempts were made to create poly(vinyl ether) acceptors for halogen bonding, but efforts have not yet produced materials that are well-suited for the formation of SPN. Early efforts to create a bifunctional charge transfer agent/initiator for a RAFT/living cationic polymerization system mainly produced unwanted products and the sample could not be readily purified. Subsequent efforts to do post-polymerization reactions are still in the early stages and have not yet produced results.

Halogen bonding was observed, using  $^{19}\text{F}$ NMR spectroscopy, in all samples containing the halogen bonding vinyl ether units. When using triethylamine (a single-point acceptor), the monomer species showed greater halogen bonding ability than the polymer species. When using tris[2-(dimethylamino)ethyl]amine ( $\text{Me}_6\text{TREN}$ ) (a four-point acceptor), however, a reverse trend was noted and polymer species showed superior halogen bonding ability. This encouraging result indicated that polymer-polymer interactions will be the most effective in forming supramolecular materials based on halogen bonding. Star-shaped polymers showed a reduced halogen bonding ability, but this is due to steric hinderance and formation of block star-shaped polymers should counter this effect.

### 今後の見通し

There is still much research left to do to effectively develop SPN based on halogen bonding poly(vinyl ether)s. In particular, active research is continuing on the development of poly(vinyl ether)s that function as acceptors for halogen bonding. A variety of post-polymerization reactions are currently under consideration. Additionally, development of an even wider range of polymer structures using the halogen bonding vinyl ethers is also planned. Finally, while halogen bonding was observed, formation of self-assembly structures was not achieved during this grant period; with appropriate acceptors creation of self-assembly structures and investigation of conditions that facilitate this is planned.