ChemComm

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c5cc02382c

Received 21st March 2015,
Accepted 29th April 2015

DOI: 10.1039/c5cc02382c

www.rsc.org/chemcomm

Utilization of a Meldrum's acid towards functionalized fluoropolymers possessing dual reactivity for thermal crosslinking and post-polymerization modification†

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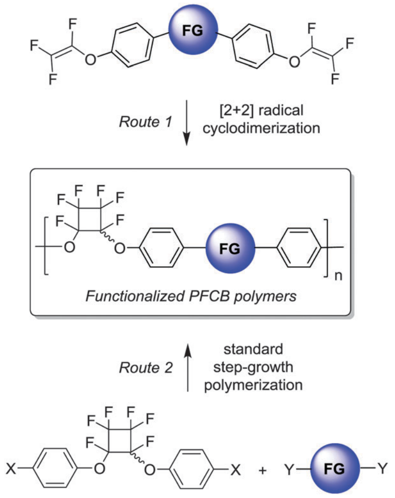
New thermally cross-linkable and/or post-functionalizable perfluorocyclobutyl (PFCB) polymers containing Meldrum's acid moieties have been successfully prepared *via* the thermal cyclopolymerization of a new Meldrum's acid functionalized aromatic trifluorovinyl ether (TFVE) monomer.

Perfluorocyclobutyl (PFCB) aryl ether polymers are a class of high value-added, tailorable fluoropolymers with a combination of many desired properties, such as processability with common solvents, excellent thermal and chemical stability, low dielectric values, and high fidelity micro-moulding replication.[1] Due to these desired properties, PFCB aryl ether polymers have demonstrated many applications such as photonics,[2] electro-optic materials,[3] proton exchange membranes,[4] hybrid composites,[5,6] and hole-transport materials.[7,8]

Typically, PFCB aryl ether polymers can be easily prepared as thermoplastics or thermosets by heating the aryl trifluorovinyl ether (TFVE) di- or tri-functional monomers or comonomers in the bulk or in solution above 150 °C *via* catalyst-free, step-growth cyclopolymerization processes.[1,9] By simply optimizing time and temperature parameters, the molecular weights of PFCB aryl ether polymers can be easily controlled which is a key feature to bulk material fabrication. Introduction of functionalities into the PFCB aryl ether polymer backbone is used to tailor their applications. Generally, functional PFCB aryl ether polymers can be prepared by direct polymerization of functional aryl TFVE monomers *via* radical [2+2] cycloaddition reaction (route 1) or PFCB aryl ether monomers with functional monomers *via* condensation reactions (route 2) as shown in Scheme 1. Due to the difficulty in the synthesis of complex functional aryl TFVE monomers and toleration of functional groups during polymerization processes, alternative strategies are highly desired in order to expand the pool PFCB aryl ether polymers.



Scheme 1 Preparation of PFCB aryl ether polymers from two common step-growth routes for functional group (FG) inclusion.

Meldrum's acid chemistry has been widely used in organic synthesis for decades.[10–13] Recently, Meldrum's acid derivatives have been successfully incorporated into a variety of polymers as both synthetic building blocks and thermolytic precursors to dialkyl ketenes.[14–18] Thermal treatment of polymers containing 5,5-disubstituted Meldrum's acid groups resulted in the loss of acetone and carbon dioxide, thereby yielding dialkyl ketenes which were used to cross-link the polymer chain *via* [2+2] dimerization and/or introduce various functional groups to the polymer side chain *via* nucleophilic addition.[19] Meldrum's acid and the resulting ketene would provide a novel and effective strategy to tandemly post-functionalize and/or cross-link PFCB aryl ether polymers thereby further expanding their applications. The Meldrum's acid functionalized aryl TFVE monomer **5** (Scheme 2) and subsequent PFCB aryl ether polymer/copolymer **6**/**7** undergoes thermoset **9** formation or affords a post-functionalized

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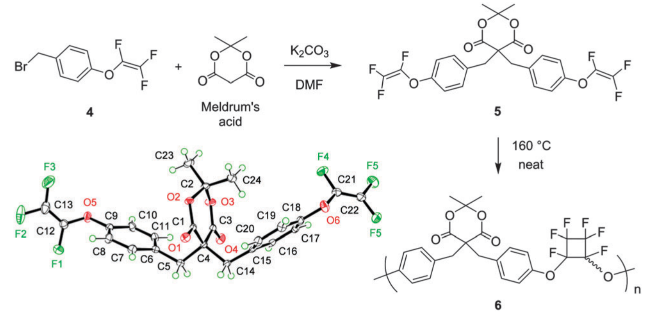
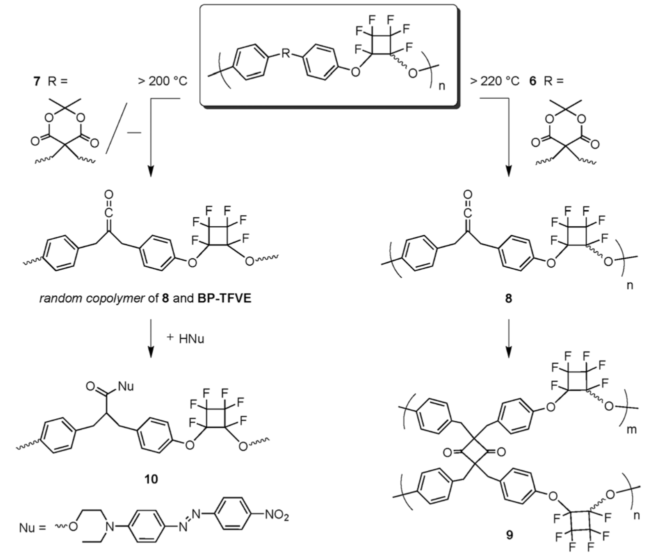
† Electronic supplementary information (ESI) available: Spectroscopic characterization, ^{1}H, ^{13}C, ^{19}F NMR, and X-ray crystallographic information. CCDC 1053394. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc02382c



Scheme 2 Synthesis of Meldrum's acid functionalized aryl TFVE **5** (with ORTEP structure, as shown 50% probability) and corresponding linear PFCB aryl ether homopolymer **6**.



Scheme 3 Synthesis of PFCB aryl ether polymers **6**, **7**, **9**, and **10** derived from monomer **5**.

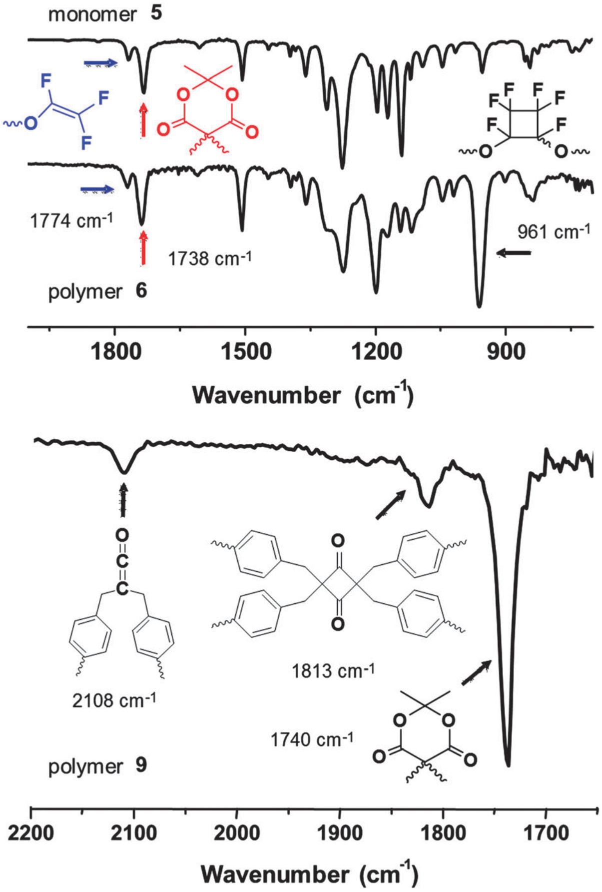


Fig. 1 ATR-FTIR spectra of monomer **5** and polymers **6** and **9**.

thermoplastic **10** (Scheme 3). To our knowledge, this dual reactivity is the first demonstrated example for a fluoropolymer and can be easily applied to other momomeric motifs.

The newly designed Meldrum's acid functionalized aryl TFVE monomer **5** was synthesized in a good isolated yield (80%) by simple alkylation of Meldrum's acid with 4-trifluorovinyl benzyl bromide **4** by following standard procedure in Scheme 2.[20] A single crystal X-ray diffraction study was carried out on monomer **5** and the molecular structure is also shown Scheme 2 inset. Experimental parameters as well as packing views are provided in the ESI.† PFCB aryl ether homopolymer **6** can be prepared *via* the thermal cyclopolymerization of monomer **5** at 160 °C. The polymerization temperature is a critical parameter in order to achieve PFCB aryl ether polymer containing Meldrum's acid which should be high enough to activate the polymerization process but low enough to avoid the thermolysis of Meldrum's acid groups. Heating monomer **5** at 160 °C for 8 h, the soluble oligomer of **6** was achieved with a number-average molecular weight (M_n) estimated by ^{19}F NMR end-group analysis (GPC analysis) of 4100 (3600) g mol^{-1}. A comparison of monomer **5** with polymer **6** in ATR-FTIR spectra is shown in Fig. 1 (top). After polymerization, a broad, strong absorbance of the PFCB ring breathing mode appeared at 961 cm^{-1} confirming chain extension while the characteristic absorbance at 1738 cm^{-1} corresponding to Meldrum's acid groups remained intact. Heating monomer **5** at elevated temperature of 180 °C for 8 h yielded insoluble material due to the formation of ketene *via* thermolysis of dialkyl Meldrum's acid followed by subsequent crosslinking (Fig. S13, ESI,† *vida infra*).

ATR-FTIR analysis (Fig. 1, bottom) after heating polymer **6** at elevated temperature of 220 °C resulted in the formation of the intermediate PFCB aryl ether polymer **8** enriched with ketene. The resulting network polymer **9** *via* **8** outlined in Scheme 3 showed residual absorbance at 2108 cm^{-1} corresponding to the typical absorbance for ketenes,[18] which indicates the unreacted ketene intermediates were very stable for a long period of time at air atmosphere, and a weak absorbance at 1813 cm^{-1}, corresponding to the typical absorbance for cyclobutane-1,3-diones formed from dialkyl ketenes *via* [2+2] dimerization procedure.[18] This observation indicated a crosslinked PFCB aryl ether polymer **9** was achieved which was insoluble with no observable glass transition temperature (T_g) was observed below 260 °C due to the high cross-linking density. In order to produce processable higher molecular weight polymer with the Meldrum's acid functional groups intact, monomer **5** was copolymerized neat with commercially available biphenyl aryl trifluorovinyl ether monomer (**BP-TFVE**) at 170 °C for 24 h with a molar feed ratio 3 : 50 (**5:BP-TFVE**). Polymerization produced a soluble, film-forming copolymer **7** with an acceptable M_n of 12 000 g mol^{-1} (GPC).

Post-polymerization modification (PPM) becomes an attractive approach to effectively incorporate diverse functional groups into a single polymer precursor[21] and very few functionalized PFCB aryl polymers have been prepared by PPM.[22] In order to demonstrate PPM utility of this system, we simply heated a mixture of an *O*-nucleophile, *N*-ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo) aniline (Disperse Red 1, denoted **DR-1**) and Meldrum's acid functionalized copolymer **7** at 200 °C for 3 h which resulted in the electro-optically active functionalized polymer **10**. The successful incorporation of **DR-1** into PFCB aryl ether polymer matrix was clearly visible by the light-red colour of polymer **10** and further validated by ^{1}H NMR spectrum whereby the disappearance of the H-signals of methyl groups in the Meldrum's acid moiety at 0.65 ppm and the appearance of the characteristic peaks of three methylene–CH_2 groups in **DR-1** chromophore (Fig. S11, ESI†). ATR-FTIR spectrum of **10** further confirmed the formation of ester bond (Fig. S18, ESI†).

Differential scanning calorimetry (DSC) studies on the prepared polymers in this study reveal well-defined T_gs from their corresponding thermal responses of the first heating cycle. As showed in Fig. S19 (ESI†) (top), oligomer **6** exhibits a T_g of 90 °C, which is lower than the T_g of optimized PFCB aryl ether polymers. Polymer **10** exhibits a T_g of 120 °C, which is slightly lower than the T_g of polymer **7** due to the NLO chromophores on the side chains, which can act as a plasticizer.

Thermal gravimetric analysis (TGA) in nitrogen of PFCP aryl ether polymers **6**, **7**, and **10** all produced step-wise degradation (Fig. S19, bottom, ESI†). For polymer **6** and copolymer **7**, the first degradation event is associated with thermolysis of Meldrum's acid groups in the respective polymer matrices. Ketene forming temperatures (T_K) of polymer **6** and **7** were determined by the onset point in TGA. The clear drop in weight at around 220 °C was attributed to the loss of CO_2 and acetone as reactive ketene was concomitantly generated. The observed weight loss percentages below 250 °C in TGA thermograms were in good agreement with the theoretically calculated weight losses (*e.g.*, for polymer **6**: found 19%: calc. 19.7%). The T_K of the copolymer **7** (220 °C) was higher than that of the polymer **6** (200 °C). Because the low molecular weight polymer **6** contains a residual reactive end groups, heating polymer **6** at 200 °C induces the aryl TFVEs to undergo the exothermic cyclodimerization while inducing thermolysis of Meldrum's acid. For polymer **10**, the first step degradation mainly takes place at around 270 °C, which may be associated with the degradation of **DR-1** groups on the side chains of polymer matrix. The second step degradations of all three polymers are associated with the degradation of the main polymer chains. As expected, polymer **6** exhibits much lower thermal stability due to the low molecule weight. Both polymer **7** and **10** exhibit similar thermal stabilities and the main weight losses take place at around 450 °C with overall high char yield *ca.* 50% at 800 °C in nitrogen.

In conclusion, ketene chemistry, for the first time, has been successfully applied in a highly utilized class of tailorable fluoropolymers, PFCB aryl ether polymer. Meldrum's acid functionalized aryl TFVE monomer has been designed and synthesized by direct alkylation of Meldrum's acid with bromomethyl aryl TFVE monomer in a good yield utilizing operationally simple transformations. Meldrum's acid functionalized PFCB aryl ether homopolymer and copolymers have been successfully prepared *via* the standard thermal [2+2] cyclodimerization of aryl TFVE groups at programmable temperatures. Transformation of Meldrum's acid to ketene intermediates successfully occurred by thermolysis above 200 °C. Post-polymerization modification *via* the ketene intermediate was demonstrated by the successful incorporation of **DR-1** into PFCB polymer matrix to form a side-chain electro-optic system. The cross-linkable and/or functionalizable Meldrum's acid groups containing PFCB aryl ether polymers could be potentially useful in various active technology sectors, such as electro-optic devices and proton exchange membranes (PEMs) for fuel cells.

We would like to thank the Intel Corporation, the Welch Foundation (Grant AT-0041), the Alan G. MacDiarmid NanoTech Institute, the National Science Foundation through the Center for Energy Harvesting Materials and Systems (NSF-I/UCRC, grant 1035024), the NMR facility of chemistry department (NSF, grant CHE-1126177), and the University of Texas at Dallas for their support. STI acknowledges the Air Force Office of Scientific Research (AFOSR) for financial support.

Notes and references

1 S. T. Iacono, S. M. Budy, J. Jin and D. W. Smith, *J. Polym. Sci., Part A: Polymer Chemistry*, 2007, **45**, 5705.
2 D. W. Smith, S. Chen, S. M. Kumar, J. Ballato, C. Topping, H. V. Shah and S. H. Foulger, *Adv. Mater.*, 2002, **14**, 1585.
3 H. Ma, J. Wu, P. Herguth, B. Chen and A. K. Y. Jen, *Chem. Mater.*, 2000, **12**, 1187.
4 B. G. Kim, H.-J. Kim, J. H. Jang, E. A. Cho, D. Henkensmeier, S.-K. Kim, I.-H. Oh, S.-A. Hong and T.-H. Lim, *Polym. Intern.*, 2011, **60**, 685.
5 J. Park, J.-M. Oh, S. E. Creager and D. W. Smith, Jr., *Chem. Commun.*, 2012, **48**, 8225.
6 S. T. Iacono, S. M. Budy, D. W. Smith and J. M. Mabry, *J. Mater. Chem.*, 2010, **20**, 2979.
7 B. Lim, J.-T. Hwang, J. Y. Kim, J. Ghim, D. Vak, Y.-Y. Noh, S.-H. Lee, K. Lee, A. J. Heeger and D.-Y. Kim, *Org. Lett.*, 2006, **8**, 4703.
8 B. Lim, Y.-C. Nah, J.-T. Hwang, J. Ghim, D. Vak, J.-M. Yun and D.-Y. Kim, *J. Mater. Chem.*, 2009, **19**, 2380.
9 D. A. Babb, B. R. Ezzell, K. S. Clement, W. F. Richey and A. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 3465.
10 A. S. Ivanov, *Chem. Soc. Rev.*, 2008, **37**, 789.
11 V. Lipson and N. Gorobets, *Mol. Diversity*, 2009, **13**, 399.
12 A. M. Dumas and E. Fillion, *Acc. Chem. Res.*, 2009, **43**, 440.
13 H. McNab, *Chem. Soc. Rev.*, 1978, **7**, 345.
14 F. A. Leibfarth, Y. Schneider, N. A. Lynd, A. Schultz, B. Moon, E. J. Kramer, G. C. Bazan and C. J. Hawker, *J. Am. Chem. Soc.*, 2010, **132**, 14706.
15 S. Cheawchan, Y. Koyama, S. Uchida and T. Takata, *Polymer*, 2013, **54**, 4501.
16 H. Jung, F. A. Leibfarth, S. Woo, S. Lee, M. Kang, B. Moon, C. J. Hawker and J. Bang, *Adv. Funct. Mater.*, 2013, **23**, 1597.
17 J. Kim, E.-H. Kang and T.-L. Choi, *ACS Macro Lett.*, 2012, **1**, 1090.
18 F. A. Leibfarth, M. Kang, M. Ham, J. Kim, L. M. Campos, N. Gupta, B. Moon and C. J. Hawker, *Nat. Chem.*, 2010, **2**, 207.
19 F. A. Leibfarth and C. J. Hawker, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 3769.
20 H.-C. Liou, P. S. Ho and A. McKerrow, *J. Polym. Sci., Part B: Polym. Phys.*, 1998, **36**, 1383.
21 M. A. Gauthier, M. I. Gibson and H.-A. Klok, *Angew. Chem., Int. Ed.*, 2009, **48**, 48.
22 K. J. Zhu, S. T. Iacono, S. M. Budy, J. Y. Jin and D. W. Smith, Jr., *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1887.