Macromolecular Rapid Communications
www.mrc-journal.de

Non-Tacky Fluorinated and Elastomeric STEM Networks

Julia Cuthbert, Michael R. Martinez, Mingkang Sun, Jacob Flum, Lingchun Li, Mateusz Olszewski, Zhenhua Wang, Tomasz Kowalewski, and Krzysztof Matyjaszewski**

Soft, elastomeric, non-tacky polymer networks are synthesized by reversible deactivation radical polymerization (RDRP). First, the pristine, structurally tailored and engineered macromolecular (STEM) networks are synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization and incorporated an atom transfer radical polymerization (ATRP) inimer into the network. Subsequently, poly(*n*-butyl acrylate) (PBA) and/or poly(octafluoropentyl acrylate) (POFPA) side chains are grafted from the network by photo-induced ATRP. These low glass transition temperature side chains produced soft materials (E = 104–178 kPa). However, only the POFPA-containing networks are also non-tacky. The fluorine content and material properties are investigated by dynamic mechanical analysis, elemental analysis, spectroscopy, and contact angle measurements.

Since the invention of polytetrafluoroethylene (PTFE) in 1938, fluoropolymers have been recognized for their many excellent properties. Fluoropolymers are hydrophobic and lipophobic, and have low surface energy, low refractive index, good weatherability, and high thermal and chemical stabilities.[1,2] All these qualities make them attractive for new functional, elastomeric materials. Moreover, recent reports have demonstrated successful polymerization of semi-fluorinated (meth)acrylates by photo-induced polymerization.[3–5]

Despite the advantages of such materials, there are relatively few reports of fluorinated elastomers,[6] and much of the research focus has been on fluorinated polymers specifically for surface functionalization.[7,8] For instance, semi-fluorinated acrylates were used to coat previously synthesized poly(divinylbenzene) networks in order to reduce ice adhesion.[8] Fluorinated monomers have also been used as additives in polyurethane elastomers.[9–11] A novel fluorinated thermoplastic polyurethane (FTPU) elastomer was prepared and mixed with poly(*n*-butyl acrylate) (PBA) as a softening agent.[6] Other soft, elastomeric materials have been designed by mixing fluorine and silicon to make polysiloxane-poly(fluorinated acrylate) interpenetrating polymer networks.[12] The Kern group also reported fluorinating natural rubber films post-synthesis using fluorine gas in a batch reactor method.[13]

Our group has developed "transformable" materials; structurally tailored and engineered macromolecular (STEM) networks.[14–18] These STEM networks are polymer networks containing latent initiator sites (inimers), which are available for controlled post-synthesis modifications. Our focus had been on grafting PBA side chains from the networks by photo-induced atom transfer radical polymerization (photo-ATRP),[19–22] which allowed for post-synthesis transformation into soft elastomeric materials.[15,23,24] The low T_g PBA side chains acted as small molecule plasticizers covalently attached to the STEM network.[16,24]

A limitation of this approach, however, was that PBA acts as a pressure sensitive adhesive (PSA).[25,26] PSAs are low modulus, viscoelastic materials that adhere to surfaces under light pressure.[26,27] Although the incorporation of PBA decreased the STEM networks' modulus, it also made them tacky at room temperature. Given this, the network samples were challenging to work with because they stuck to many surfaces, including gloves, metal tweezers, glass, and rheological measurement instrumentation. This difficulty inspired us to use a semi-fluorinated acrylate with a low T_g instead of tacky PBA. The semi-fluorinated acrylate was expected to plasticize the STEM network and lower its surface energy (much like Teflon) to make soft, non-tacky materials. There are other methods to produce soft and non-tacky polymeric materials, such as plasticizing renewable materials with dodecane[28] or using biopolymers like β-keratin.[29] However, the semi-fluorinated monomer chosen was octafluoropentyl acrylate (OFPA) for two reasons. First, photo-ATRP of semi-fluorinated acrylates has been reported with very good control.[3] Second, poly(octafluoropentyl acrylate) (POFPA) has one of the lowest T_g of the semi-fluorinated acrylates at −35 °C,[3,30] making it the best comparison with PBA.

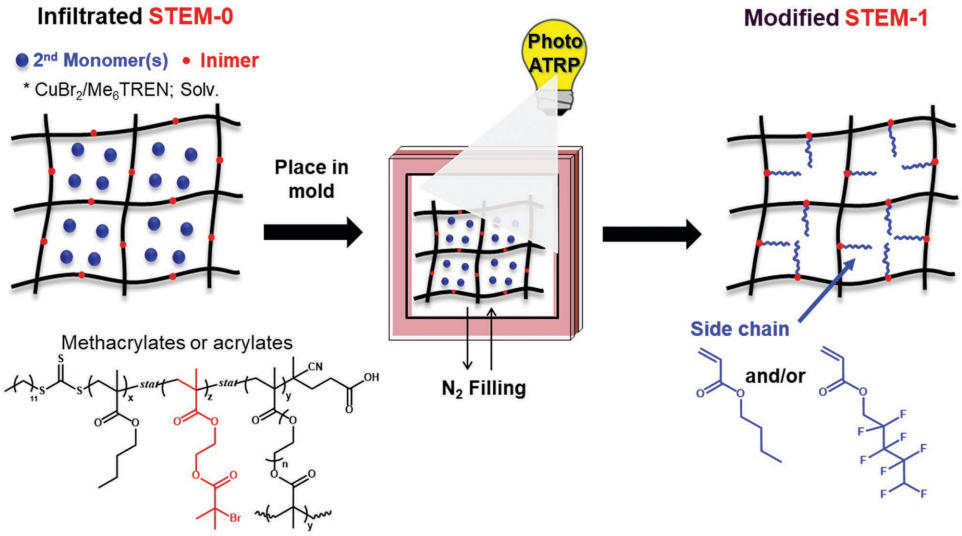
In this paper, we demonstrated that the STEM networks containing semi-fluorinated polymer side chains not only behaved as soft elastomers, but also were non-tacky. It is anticipated that the described soft, non-sticky fluorinated network will be applicable to functional materials and soft coatings. For example, the networks could be used as a skin mimetic outer layer for soft robotics.

The STEM network architecture is similar to polymer brushes, which consist of a backbone with dangling side

J. Cuthbert, M. R. Martinez, M. Sun, J. Flum, Dr. L. Li, M. Olszewski, Z. Wang, Prof. T. Kowalewski, Prof. K. Matyjaszewski
Department of Chemistry
Carnegie Mellon University
4400 Fifth Avenue, Pittsburgh, PA 15213, USA
E-mail: tomek@andrew.cmu.edu; km3b@andrew.cmu.edu
The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.201800876.

DOI: 10.1002/marc.201800876

Macromolecular Rapid Communications
www.mrc-journal.de



Scheme 1. The STEM-0 networks and post-synthesis modifications. The STEM-0 networks were previously prepared by RAFT polymerization and then infiltrated with a second monomer (BA or OFPA), copper catalyst, and solvent. The swollen gel was placed in a degassed mold and polymer side chains were grafted from the network by photo-ATRP to produce an STEM-1 network.

chains. The primary STEM-0 networks were prepared by copolymerizing the backbone (meth)acrylate monomer, inimer ((meth)acrylate with pendent ATRP initiator), and difunctional oligo(ethylene glycol) dimethacrylate crosslinker by thermally mediated reversible addition–fragmentation chain transfer (RAFT) polymerization (**Scheme 1**; Scheme S1, Supporting Information). In this strategy, the inimer was incorporated directly into the STEM network through its (meth)acrylate group and the α–bromoisobutyrate (iBBr) functional group was available for subsequent orthogonal modifications by photo-ATRP.[15,24] Two STEM-0 networks were prepared: *n*-butyl methacrylate (BMA), methacrylate inimer (HEMA-iBBr), and methacrylate crosslinker ($PEO_{750}DMA$) (Scheme S1, Supporting Information); and *n*-butyl acrylate (BA), acrylate inimer (HEA-iBBr), and acrylate crosslinker ($PEO_{700}DA$) (Scheme S1, Supporting Information).

The STEM-0 networks were infiltrated with the second monomer (BA and/or OFPA), catalyst, and solvent. 2,2,3,3,4,4,5,5-Octafluoro-1-pentanol (OFP-OH) was utilized as a solvent to solubilize all components of the reaction mixture while preventing deleterious transesterification reactions from altering sidechain structure, which have both been well-reported issues faced in related works.[3,31] The typical molar equivalents were: second monomer/inimer/$CuBr_2$/Me_6TREN = 30–50/1/0.02/0.12 and the target solution mass was ten times that of the pristine, dry STEM-0 network (Supporting Information). The side chains were then grafted from the network by photo-ATRP (λ = 365 nm; 10 mW cm^{-2} for 5.5 h). To ensure uniform light exposure on both sides, the network was rotated every 30 min. It should be noted that the STEM-0 gels were compatible with the BA monomer infiltration solution, swelling approximately nine times their original weight (Table S1, Supporting Information). In contrast, the OFPA monomer (Table S1, Supporting Information) was less compatible with the network and the STEM-0 network only swelled approximately three to four times. Three different types of side chains were grafted from three STEM-0 gel samples: PBA; PBA-*stat*-POFPA; and POFPA to produce STEM-1 networks (**Table 1**). The weight percent (wt%) of side chains in the networks was estimated by gravimetry (Table 1) and the theoretical degree of

Table 1. The STEM-0 and STEM-1 networks synthesized showing side chain composition, monomer conversion, percent by weight, and degree of polymerization (DP).

STEM-0 network	Label	Side chain	Wt% side chains[a] [%]	DP_{Theo}[b] side chain	Wt% F Theo[b] [%]	Wt% F elemental analysis[c] (±0.4%) [%]
PBMA-*stat*-inimer-*stat*- crosslinker	PBMA_BA	PBA	79	19	0	N/A
	PBMA_BA/OFPA	PBA-*stat*-POFPA	81	Total 14	37	26.9
	PBMA_OFPA	POFPA	69	5	36	32.3
PBA-*stat*-inimer-*stat*- crosslinker	PBA_BA	PBA	84	28	0	N/A
	PBA_BA/OFPA	PBA-*stat*-POFPA	76	Total 10	35	19.6
	PBA_OFPA	POFPA	65	4	32	36.3

[a]Gravimetric analysis; [b]Section S4.1, Supporting Information. PBA-*stat*-POFPA side chains assume equimolar side chain incorporation of BA and OFPA. It is probable that less OFPA was infiltrated due to incompatibility with the network (Table S1, Supporting Information); [c]Determined by ion concentration measurement (ISE).

polymerization (DP_{theo}) was also calculated (Supporting Information). The fluorine content was also determined by elemental analysis.

By simple tactile examination, the dry STEM-1 networks containing pure POFPA side chains (PBMA_OFPA, PBA_OFPA) were noticeably non-sticky and easier to handle compared to their PBA side chain counterparts (**Figure 1**A; Table S2, Supporting Information). For comparison, the STEM networks were prepared using two distinctly different primary STEM-0 networks: soft, tacky (PBA) and stiffer, non-tacky (PBMA). To assess the impact of PBA and POFPA side chains on the STEM-1 adhesion, a standard probe tack test was performed using a parallel plate fitted Anton-Parr rheometer (see Supporting Information) (Figure 1B,C).[27,32] The samples were affixed to the bottom plate using double-sided tape. The top stainless-steel parallel plate was brought into contact with each sample for 10 s under a constant load of 1 N. Then the plate was retracted at 0.1 mm s^{-1} while the displacement and normal force were recorded. The separation of the plate and the sample was indicated by the decrease of force to 0 N without any further changes as retraction proceeded. A recorded negative normal force indicated resistance to the top plate being raised and continued contact between the sample and plate, which is evidence of tack (PBMA_BA in Figure 1B and STEM-0 PBA, PBA_BA, PBA_BA/OFPA in Figure 1C).

The tack tests provided quantitative data showing that the POFPA side chains prevented the networks from sticking to other surfaces (Figure 1B,C blue lines). For the PBMA network, the pristine STEM-0 was non-tacky (Figure 1B black line) and there was no resistance to retraction. The PBMA network was rigid at room temperature (22 °C), and for this reason, on retracting the top plate, the normal force abruptly decreased to 0 N. In contrast, the more deformable, compressed STEM-1 networks took several seconds to recover to 0 N as the plate retracted. Importantly, when only PBA side chains were grafted, PBMA_BA, PBA_BA, the STEM-1 networks exhibited marked tackiness, with the average minimum force reaching –0.17 and –0.23 N respectively (Figure 1B,C red lines; Table S2, Supporting Information). Due to fluorine's low surface energy, no significant tack was observed for the network grafted with POFPA side chains (Figure 1B,C blue lines; Table S2, Supporting Information). Networks with statistical copolymer side chains displayed some residual tack (PBMA_BA/OFPA; PBA_BA/OFPA; Figure 1B,C green lines; Table S2, Supporting Information). In the case of PBMA_BA/OFPA, the residual tack (average minimum force = –0.11 N; Table S2, Supporting Information) was less than the PBMA_BA network, indicating that the material behavior was dominated by the fluorinated groups (Figure 1B blue lines).

Further, it was observed that the primary network backbone had a pronounced effect on the modified STEM-1 network's final properties. For instance, when the two STEM-0 networks, tacky PBA and non-tacky PBMA, were grafted with POFPA side chains, no significant tack was observed. PBA side chains naturally resulted in tacky STEM-1 networks. However, when the network scaffold was tacky PBA, the semi-fluorinated groups in the statistical copolymer side chains were insufficient to eliminate tack.

The compression test results confirmed that the addition of OFPA to the STEM-1 networks produced not only non-tacky materials, but also soft, elastomeric ones (Figure 1D,E). This is particularly important since it demonstrated that the semi-fluorinated side chains do act as diluents and soften the networks in place of traditional small molecule solvents as intended. All three side chain compositions plasticized the rigid PBMA STEM-0 network and decreased the compression Young's modulus by approximately an order of magnitude (Figure 1D). In contrast, no additional softening was observed after the introduction of side chains to the soft PBA STEM-0 network (Figure 1D) as the network was already made from a low T_g polymer.

In addition, the networks were characterized by dynamic mechanical analysis (DMA) temperature sweeps (Figure 1F,G). The storage modulus (G') (the elastic component shear modulus) and the damping factor, tan (δ) (G''/G') were recorded. Except for the PBMA STEM-0, all the other STEM networks reached their rubbery plateau at room temperature. The rubbery plateau G' values were on the order of 10^3–10^4 Pa, in agreement with previous supersoft networks with similar macromolecular architecture.[24]

Tan (δ) measurements (Figure 1F,G [bottom half]) were particularly useful for assessing the impact of grafted side chains on viscoelasticity and for determining the glass transition temperature (T_g) by finding the local maxima in the tan (δ) versus temperature plots. In order to determine the T_g range, three linear analogues of the polymer side chains (target DP = 50) were synthesized (Figures S2–S5, Supporting Information) and the T_g was measured (Figure S6, Supporting Information): PBA = –46.6 °C; POFPA = –34.8 °C; PBA-*stat*-POFPA = –45.6 °C and = –38.8 °C. The PBMA_BA tan (δ) results were in good agreement with previous observations.[24] A sharp peak at approximately –40 °C corresponding to the PBA side chains and a broader peak over a higher temperature range corresponding to the plasticized backbone were observed (Figure 1F,G red lines). Both PBMA_OFPA and PBA_OFPA showed very broad tan (δ) feature, resulting from the comparatively short side chains and from plasticized backbone blending (Figure 1F,G blue lines). Finally, as with the linear models, STEM-1 networks with PBA-*stat*-POFPA side chains had tan (δ) local maxima values in between the pure PBA and POFPA samples (Figure 1F,G green lines).

The surface properties were also characterized. Elemental analysis by X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX) were used to provide further evidence of the incorporation and distribution of OFPA. For all STEM-1 networks grafted with semi-fluorinated side chains, the XPS survey scan revealed the presence of fluorine (binding energy ≈700 eV) on the network surface, which was not observed in the non-fluorinated networks (Figures S7,S8, Supporting Information). XPS F1s scans on the semi-fluorinated networks confirmed fluorine peaks (688–689 eV) (**Figure 2**A,B). The XPS C1s scans also revealed CF_2 bonds (291 eV) (Figures S9, S10, Supporting Information). EDX imaging of surfaces exposed by sectioning of the samples revealed the consistent distribution C, O, F. The networks were also cut and EDX mapping was performed on the cross-sections. This revealed the consistent elemental distribution of C, O, F across all the

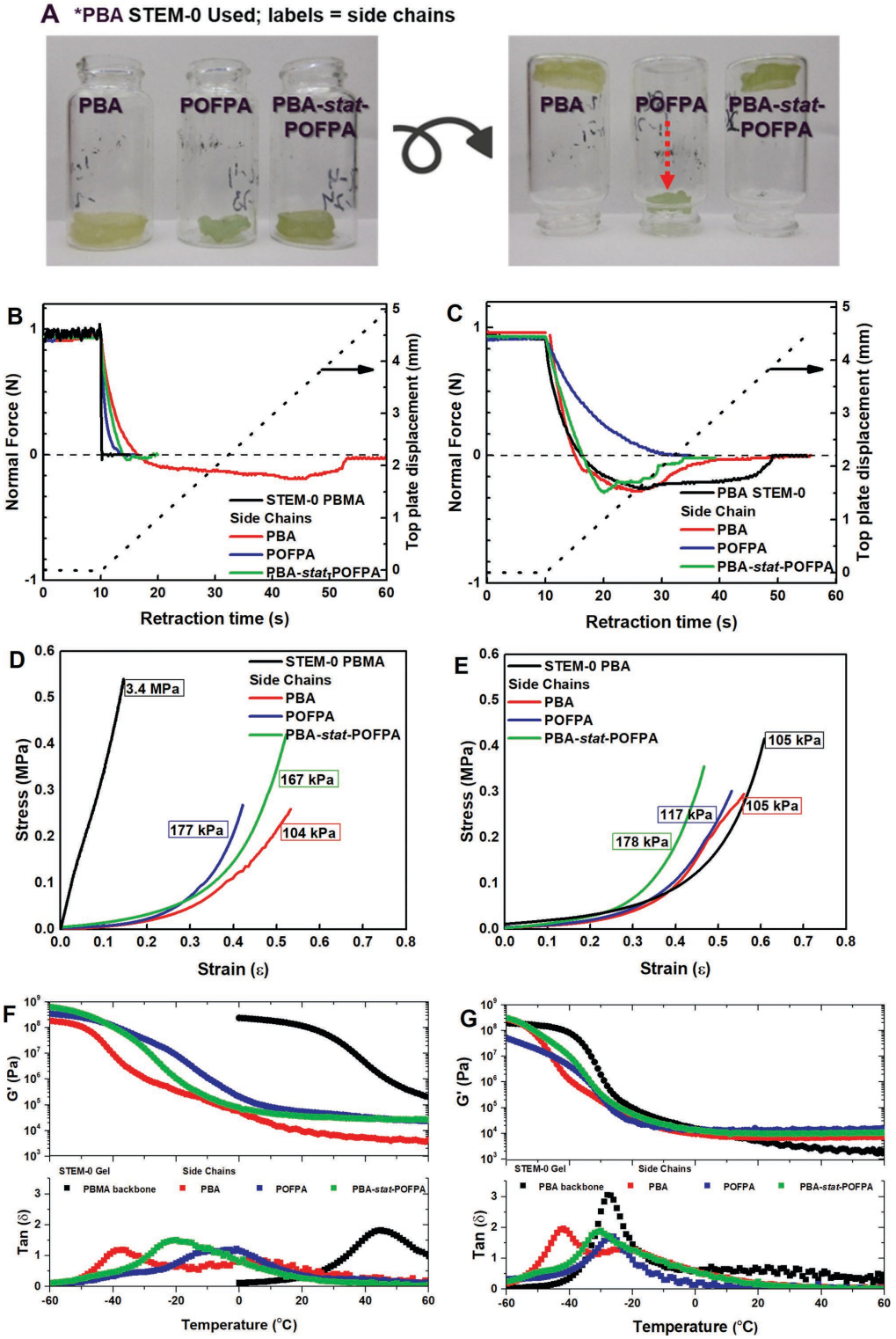


Figure 1. A) The qualitative tack demonstration of the STEM-1 networks (PBA scaffold) in glass vials. For all figures, the black lines/shapes = STEM-0 networks, and for the STEM-1 networks, red = PBA side chains, blue = POFPA side chains, and green = PBA-*stat*-POFPA side chains. B) STEM-0 PBMA and C) STEM-0 PBA, the force versus time (solid lines) and the top plate displacement (dashed line) for the tack tests using stainless-steel parallel plates. D) STEM-0 PBMA and E) STEM-0 PBA, the stress–strain curves under compression with Young's modulus values in boxes. F) PBMA STEM networks and G) PBA STEM networks, the temperature dependent behavior of the storage modulus, G', and tan (δ) at a constant angular frequency of $\omega = 1$ rad s^{-1} and shear strain amplitude (γ) = 0.1%.

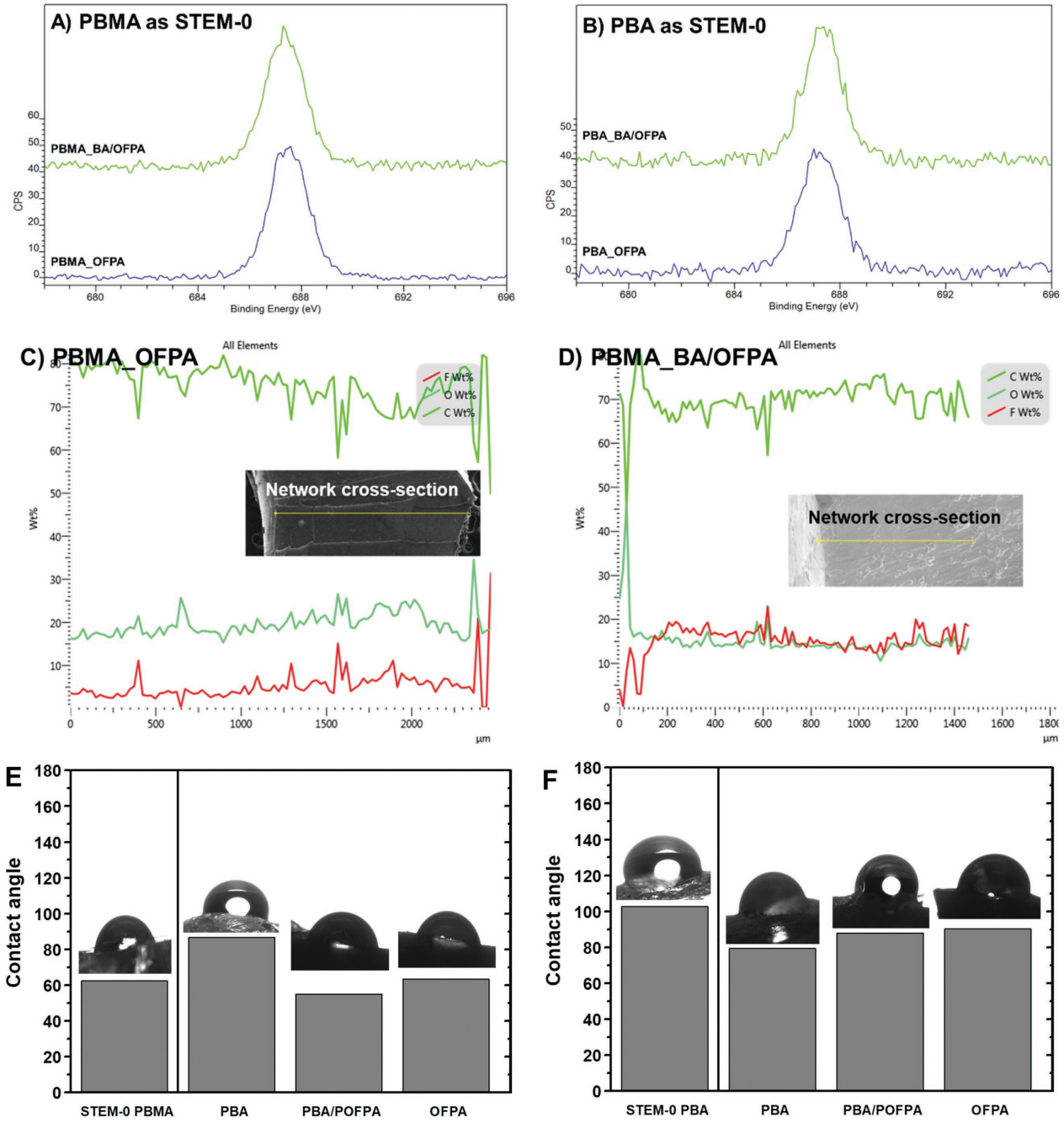


Figure 2. The high-resolution XPS F1s spectra of the A) semi-fluorinated PBMA and B) PBA STEM-1 networks. The EDX surface mapping of C) PBMA_OFPA and D) PBMA_BA/OFPA cross-sections showing the elemental wt% of F, O, and C. The yellow line represents the EDX line scan. (For the PBA STEM network scans, see Figure S11, Supporting Information.) The contact angles of a water drop on the STEM network surfaces: E) PBMA and F) PBA.

samples pointing to the relatively uniform incorporation of the second monomer(s)(Figure 2C,D; Figure S11, Supporting Information). More importantly, it indicated that the UV light–induced photo-ATRP throughout the network rather than just from the surface. Finally, contact angle measurements showed that the STEM networks retained hydrophobicity (Figure 2E,F).

Tunable, soft elastomeric, non-tacky materials were prepared by grafting semi-fluorinated side chains from two types of STEM networks: either soft (PBA) or semi-rigid (PBMA) backbones. Incorporation of these side chains eliminated the tacky character of the materials and acted as diluents in the case of the PBMA network. The STEM networks were prepared by RAFT polymerization while simultaneously incorporating an ATRP inimer for the second stage photo-induced network modifications. Both PBA and POFPA side chains were grafted from the networks. Although both produced soft materials

(E = 104–178 kPa), the PBA STEM-1 networks were tacky whereas the lower surface energy C—F bonds resulted in non-sticky networks. Spectroscopic analysis further confirmed fluorine content and showed uniform distribution throughout the network. These materials could be applied to fabrication of soft, non-tacky coatings and other functional materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Financial support from the Department of Energy (grant ER45998) is gratefully acknowledged. The NMR facility at CMU was partially supported by NSF grants CHE-9808188, CHE-1039870 and CHE-1726525. The Materials Characterization Facility at CMU supported by grant MCF-677785. We would also like to thank Dr. Adam Wise (CMU Materials Characterization Facility).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

atom transfer radical polymerization, elastomers, polymer networks, semi-fluorinated, macromolecular gels

Received: December 2, 2018
Revised: January 24, 2019
Published online: February 10, 2019

[1] M. Guerre, C. Taplan, R. Nicolay, J. M. Winne, F. E. Du Prez, *J. Am. Chem. Soc.* **2018**, *140*, 13272.
[2] R. Bongiovanni, G. Malucelli, M. Sangermano, A. Priola, *J. Fluorine Chem.* **2004**, *125*, 345.
[3] E. H. Discekici, A. Anastasaki, R. Kaminker, J. Willenbacher, N. P. Truong, C. Fleischmann, B. Oschmann, D. J. Lunn, J. Read de Alaniz, T. P. Davis, C. M. Bates, C. J. Hawker, *J. Am. Chem. Soc.* **2017**, *139*, 5939.
[4] Q. Quan, H. Gong, M. Chen, *Polym. Chem.* **2018**, *9*, 4161.
[5] X. Yao, S. S. Dunn, P. Kim, M. Duffy, J. Alvarenga, J. Aizenberg, *Angew. Chem., Int. Ed.* **2014**, *53*, 4418.
[6] T. Liu, L. Ye, *J. Fluorine Chem.* **2010**, *131*, 36.
[7] R. F. Brady, C. L. Aronson, *Biofouling* **2003**, *19*, 59.
[8] H. Sojoudi, G. H. McKinley, K. K. Gleason, *Mater. Horiz.* **2015**, *2*, 91.
[9] P. Game, D. Sage, J. P. Chapel, *Macromolecules* **2002**, *35*, 917.
[10] C. Tonelli, T. Trombetta, M. Scicchitano, G. Simeone, G. Ajroldi, *J. Appl. Polym. Sci.* **1996**, *59*, 311.
[11] N. Li, F. Zeng, Y. Wang, D. Qu, W. Hu, Y. Luan, S. Dong, J. Zhang, Y. Bai, *RSC Adv.* **2017**, *7*, 30970.
[12] V. Darras, O. Fichet, F. Perrot, S. Boileau, D. Teyssié, *Polymer* **2007**, *48*, 687.
[13] S. Schlögl, R. Kramer, D. Lenko, H. Schröttner, R. Schaller, A. Holzner, W. Kern, *Eur. Polym. J.* **2011**, *47*, 2321.
[14] A. Beziau, A. Fortney, L. Y. Fu, C. Nishiura, H. B. Wang, J. Cuthbert, E. Gottlieb, A. C. Balazs, T. Kowalewski, K. Matyjaszewski, *Polymer* **2017**, *126*, 224.
[15] J. Cuthbert, A. Beziau, E. Gottlieb, L. Fu, R. Yuan, A. C. Balazs, T. Kowalewski, K. Matyjaszewski, *Macromolecules* **2018**, *51*, 3808.
[16] A. Mpoukouvalas, W. W. Li, R. Graf, K. Koynov, K. Matyjaszewski, *ACS Macro Lett.* **2013**, *2*, 23.
[17] H. He, S. Averick, P. Mandal, H. Ding, S. Li, J. Gelb, N. Kotwal, A. Merkle, S. Litster, K. Matyjaszewski, *Adv. Sci. (Weinh)* **2015**, *2*, 1500069.
[18] M. Chen, Y. Gu, A. Singh, M. Zhong, A. M. Jordan, S. Biswas, L. T. J. Korley, A. C. Balazs, J. A. Johnson, *ACS Cent. Sci.* **2017**, *3*, 124.
[19] D. Konkolewicz, K. Schroder, J. Buback, S. Bernhard, K. Matyjaszewski, *ACS Macro Lett.* **2012**, *1*, 1219.
[20] X. C. Pan, M. A. Tasdelen, J. Laun, T. Junkers, Y. Yagci, K. Matyjaszewski, *Prog. Polym. Sci.* **2016**, *62*, 73.
[21] K. Matyjaszewski, N. V. Tsarevsky, *J. Am. Chem. Soc.* **2014**, *136*, 6513.
[22] J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614.
[23] W. F. M. Daniel, J. Burdyńska, M. Vatankhah-Varnoosfaderani, K. Matyjaszewski, J. Paturej, M. Rubinstein, A. V. Dobrynin, S. S. Sheiko, *Nat. Mater.* **2015**, *15*, 183.
[24] J. Cuthbert, T. Zhang, S. Biswas, M. Olszewski, S. Shanmugam, T. Fu, E. Gottlieb, T. Kowalewski, A. C. Balazs, K. Matyjaszewski, *Macromolecules* **2018**, *51*, 9184.
[25] I. Webster, *Int. J. Adhes. Adhes.* **1997**, *17*, 69.
[26] S. D. Tobing, A. Klein, *J. Appl. Polym. Sci.* **2001**, *79*, 2230.
[27] C. Costantino, C. Matteo, *Rep. Prog. Phys.* **2016**, *79*, 046601.
[28] P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, L. Leibler, *Nature* **2008**, *451*, 977.
[29] M. S. Prowse, M. Wilkinson, J. B. Puthoff, G. Mayer, K. Autumn, *Acta Biomater.* **2011**, *7*, 733.
[30] F. A. Bovey, J. F. Abere, G. B. Rathmann, C. L. Sandberg, *J. Polym. Sci.* **1955**, *15*, 520.
[31] S. R. Samanta, R. Cai, V. Percec, *Polym. Chem.* **2014**, *5*, 5479.
[32] P. Rao, T. L. Sun, L. Chen, R. Takahashi, G. Shinohara, H. Guo, D. R. King, T. Kurokawa, J. P. Gong, *Adv. Mater.* **2018**, *30*, 1801884.