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C1 Polymerization of Fluorinated Aryl Diazomethanes

Songsu Kang,† Sherilyn J. Lu,† and Christopher W. Bielawski*

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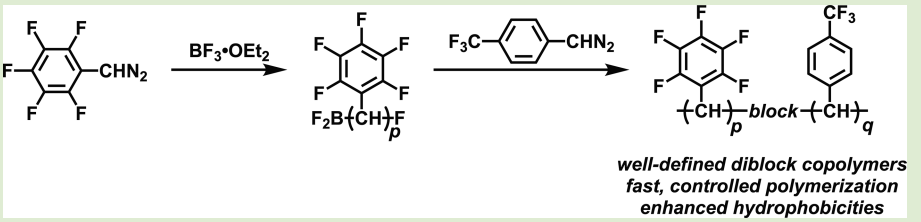

ABSTRACT: A library of fluorinated aryl diazomethanes were polymerized using $BF_3{\cdot}OEt_2$ as a catalyst. The polymerization of 2,3,4,5,6-pentafluorophenyl diazomethane was found to be controlled, permitted chain extensions, and facilitated access to a series of block copolymers. Moreover, the polymer chains grew in one carbon increments (so-called "C1 polymerizations") and, as such, afforded highly substituted polymers that featured aryl units pendant to every carbon atom of the backbone. The polymers were characterized using size exclusion chromatography, various spectroscopic techniques, and a series of static and dynamic contact angle measurements. Compared to less-substituted analogues that were prepared using typical C2 polymerization methodologies, the C1 fluorinated polymers were found to be more hydrophobic while maintaining a sufficient solubility to be processed into robust films.

Since the discovery[1,2] of poly(tetrafluoroethylene) (PTFE), fluorinated polymers have garnered widespread interest for use in applications that range from high-performance coatings[3−5] through electronics and optics[6,7] to biomedicine.[6,8] The broad utility stems from the unique properties that are intrinsic to fluorinated polymers, as they often exhibit high hydrophobicities,[1,4,9,10] high thermal stabilities,[1,4,9,10] broad chemical resistance,[1,3,4,9,10] low dielectric constants,[3,4,11] and low refractive indices.[4,12] Such properties ultimately derive from the C−F bond. Despite being highly polar, C−F bonds exhibit low polarizability, which results in low surface energies and high stability.[1,4,10] Moreover, the effects bestowed by C−F bonds can be additive:[13] fluorinated materials, particularly fluorinated polymers, often become more thermally stable,[14] more hydrophobic,[15,16] more chemically resistant,[15] and less refractive[17] as the fluorine content increases.

Fluorinated polymers are generally prepared using a "C2 polymerization" method, wherein polymer chains are grown in two carbon increments.[18−20] For example, PTFE, poly(vinylidene fluoride), and fluorinated poly(styrene) are prepared via the free radical polymerization from their constituent olefinic monomers.[3,21,22] While such methods provide access to polymers with fluorinated backbones and derivatives that feature periodic fluorinated side chains, access to highly substituted derivatives remains limited due to steric hindrance as inadvertent isomerization generally accompanies polymerization and affords ill-defined mixtures of polymer chains or effectively terminates the reaction.[23] Densely fluorinated polymers, which can be expected to amplify the favorable properties provided by C−F bonds, requires a synthetic method that installs a highly fluorinated substituent on every carbon atom of the main chain.

We envisioned the use of a "C1 polymerization" to meet the aforementioned challenge. C1 polymerizations grow polymer chains in single carbon increments[24,25] and, as such, afford access to highly substituted polymers.[24−57] For example, as shown in Scheme 1, Ray and Matthies independently demonstrated that various catalysts can be used to convert diazoethane to poly(methyl methylene). Although the corresponding C1 polymerization reactions were uncontrolled, the polymers produced feature a methyl group on every carbon atom of their backbones.[37,38] Since those early reports, emphasis has focused on the use of diazoesters as monomers in part because such compound are relatively stable and can be readily modified through variation of the pendant ester group.[24,25,29,32−36,42−53] Fluorinated diazoesters, such as 3,3,4,4,5,5,6,6,6-nonafluorohexyl diazoacetate, 2-fluorophenyl diazoacetate, and 2,6-difluorophenyl diazoacetate, have been subjected to C1 polymerization strategies;[54] however, the products obtained from these reactions are insoluble, which has thwarted characterization and utilization.

Fluorinated aryl diazomethanes are an attractive alternative monomer platform for accessing fluorinated polymers. Such

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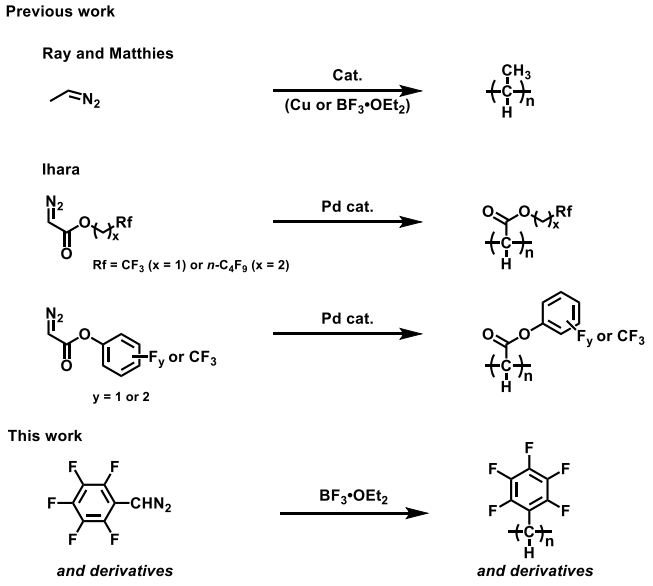
Scheme 1. C1 Polymerization of Diazo Compounds



compounds are stable, can be readily prepared and isolated under mild conditions, and are amenable to structural modification.[58] In many cases, the compounds can be synthesized on relatively large scales and are even commercially available. Fluorinated aryl diazoalkanes are also nucleophilic and known to react with Lewis acids (e.g., 4-trifluoromethylphenyl diazomethane and 2,3,4,5,6-pentafluorophenyl diazomethane).[59,60] We hypothesized that the introduction of a catalytic amount of Lewis acid to a fluorinated aryl diazoalkane should result in a spontaneous C1 polymerization reaction. Since the propagating intermediates formed in such a reaction should also be relatively stable, inadvertent disproportion or chain transfer may be suppressed and afford a controlled polymerization.

As shown in Scheme 2, a series of fluorinated phenyl diazomethane derivatives (**1**) were synthesized through modifications of known literature procedures.[61−63] Condensation of 2,4,6-triisopropylbenzenesulfonyl chloride (**2**) and hydrazine at 0 °C in THF afforded sulfonyl hydrazide **3**, which was then used to transform various aldehydes (**4**) into their corresponding *N*-tosylhydrazones (**5**).[61] Treatment of **5** with potassium hydroxide in methanol for 10 min, followed by vacuum distillation, afforded the desired fluorinated phenyl diazomethanes **1a**−**1f**.[61,62] Derivative **1g** was prepared using a different approach. First, aldehyde **4g** was synthesized from octafluorotoluene, zinc powder, tin(II) chloride, and copper(I) chloride via a Vilsmeier−Haack reaction.[63] Subsequent condensation with **3** afforded **5g**, which was hydrolyzed with sodium methoxide to give **1g**. Phenyl diazomethane[61,62] was also prepared as a control and used to compare against the fluorinated phenyl diazomethane derivatives.

With the monomers in hand, efforts were directed toward using $BF_3{\cdot}OEt_2$ to induce polymerization; key results are summarized in Table 1.[37,41,55,64] A solution of **1a** ($[\mathbf{1a}]_0$ = 0.48 M) was first treated with catalytic amounts of $BF_3{\cdot}OEt_2$ ($[\mathbf{1a}]_0/[BF_3{\cdot}OEt_2]_0$ = 100) at room temperature. While no chemical reaction was evident when the polymerization was performed in diethyl ether, a vigorous evolution of a gas,

Scheme 2. Preparation of Fluorinated Phenyl Diazomethane Derivatives (a) 1a−1f and (b) 1g

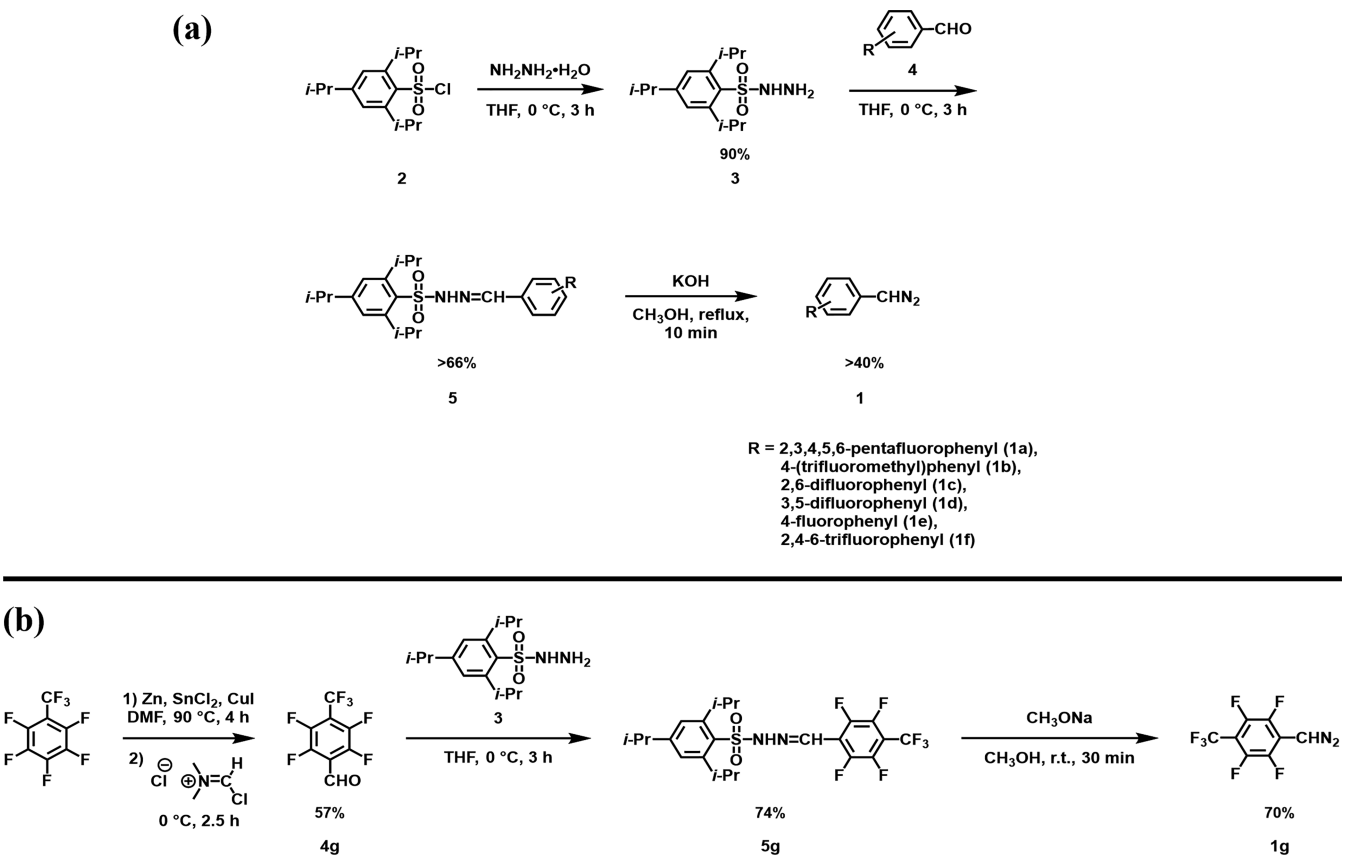


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Table 1. Summary of the Conditions That Were Used to Polymerize 1a[a]

entry	solvent	yield[b] (%)	M_{n_theory}[c] (kDa)	M_{n_exp}[d] (kDa)	$Đ$[d]
1	diethyl ether	n/r	18.0		
2	benzene	40	18.0	11.1	1.09
3	toluene	53	18.0	9.2	1.11
4	hexafluorobenzene	n/r	18.0		
5	chloropentafluorobenzene	n/r	18.0		
6	1,3-bis(trifluoromethyl)benzene	77	18.0	14.2	1.14

[a]Conditions: $[\mathbf{1a}]_0$ = 0.48 M, $[\mathbf{1a}]_0/[BF_3{\cdot}OEt_2]_0$ = 100, 10 min, r.t. [b]Isolated yield (%) after collection of the solids that precipitated upon pouring the crude reaction mixtures into a mixture of methanol and water (4:1 v/v). [c]The theoretical M_n values were based on the $[\mathbf{1a}]_0/[BF_3{\cdot}OEt_2]_0$ feed ratio and assumed quantitative conversion of monomer to polymer. [d]Determined by SEC in chloropentafluorobenzene against poly(dimethylsiloxane) standards.

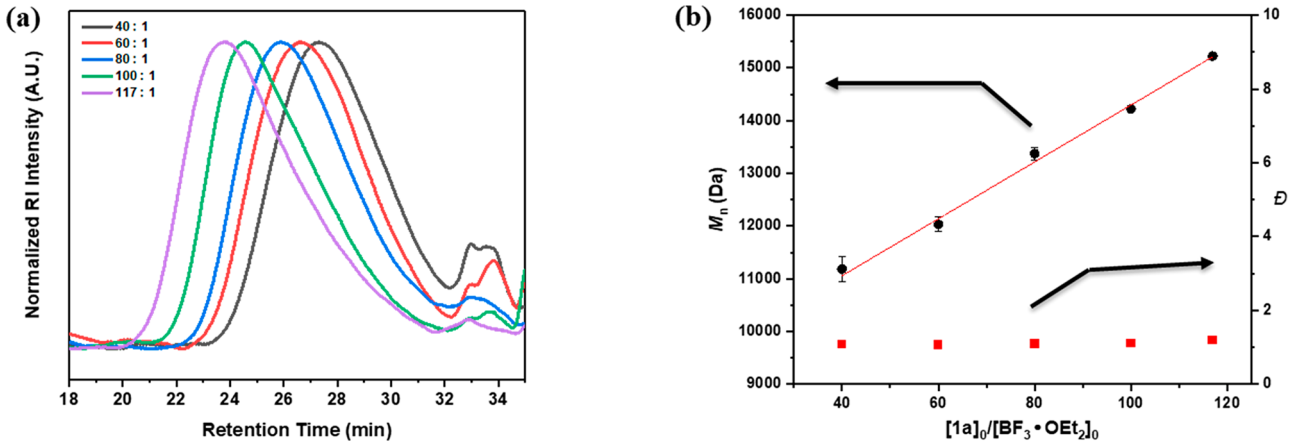

Figure 1. (a) SEC data recorded for poly(**1a**), as obtained using different initial feed ratios of monomer to catalyst (indicated). (b) Plot of M_n and $Đ$ of poly(**1a**) vs the initial monomer to catalyst feed ratio. Conditions: $[\mathbf{1a}]_0$ = 0.48 M, 1,3-bis(trifluoromethyl)benzene, 10 min, r.t. Isolated yields were typically >51%.

presumably nitrogen, was observed when benzene or toluene was used as the solvent. Fluorinated polymers have been reported to exhibit increased solubility in fluorinated solvents.[65] Therefore, the polymerization of **1a** was repeated in various fluorinated aromatic solvents to determine if any beneficial effects were observed. Although polymerization was not observed when the reactions were performed in hexafluorobenzene or chloropentafluorobenzene,[66] monomer **1a** converted to its corresponding polymer when the reaction was conducted in 1,3-bis(trifluoromethyl)benzene. Moreover, the quantity of the polymer produced was relatively high when compared to the analogous reaction that was performed in an hydrocarbon-based solvent.

At the conclusion of the polymerizations, the reaction mixtures were poured into an excess of a mixture of methanol and water (4:1 v/v).[67] The solids that precipitated were collected via filtration, dried, and then characterized using multinuclear NMR spectroscopy. Collectively, the spectroscopic data were in agreement with the structure shown for poly(**1a**). For example, in addition to a broad signal centered at 3.96 ppm (hexafluorobenzene with C_6D_6), which was assigned to the methine protons of the polymer backbone, three distinct ^{19}F NMR signals were observed at −133.97, −149.90, and −159.84 ppm (hexafluorobenzene), which were attributed to the *meta*-, *para*-, and *ortho*-F groups in the pendant aryl groups, respectively (see Figures S61 and S63). A broad ^{11}B NMR signal was also recorded at 1.94 ppm and assigned to a $-BF_2$ end group (see Figure S87).

Size exclusion chromatography is commonly used to assess the molecular weight and polydispersity of polymeric materials. However, since the fluorinated polymers were not highly soluble in the organic solvents commonly used in SEC (e.g., THF, CH_2Cl_2, etc.), a custom chromatograph that utilized chloropentafluorobenzene as the eluent was designed. Using the custom chromatograph, the M_n and polydispersity index ($Đ$) of poly(**1a**) was determined to be 14.2 kDa and 1.14, respectively. For reference, the theoretical M_n value was calculated to 18.0 kDa, assuming quantitative initiation and complete consumption of monomer.[68]

To determine if the polymerization reactions were controlled, a series of experiments that varied the initial monomer to catalyst feed ratios were undertaken in 1,3-bis(trifluoromethyl)benzene at room temperature. As shown in Figure 1a, the size-exclusion chromatograms recorded for the isolated polymers were unimodal. A linear correlation between the M_n of the isolated polymer products and the initial feed ratio was also observed, along with low $Đ$ values (Figure 1b). Collectively, these data indicated that the polymerizations permitted control, a feature that may stem from the fluoro groups on the monomers that can stabilize propagating intermediates to prevent premature decomposition. The use of fluorinated solvents was also required to ensure that solubility was sufficient over the course of the polymerization reaction.

In addition to predictable molecular weight, controlled polymerizations enable chain extensions and offer access to block copolymers.[69] To determine if the polymerizations met such criteria, a series of sequential reactions was conducted as described in Figure 2a. A solution of monomer **1a** ($[\mathbf{1a}]_0$ = 0.48 M) in 1,3-bis(trifluoromethyl)benzene was treated with

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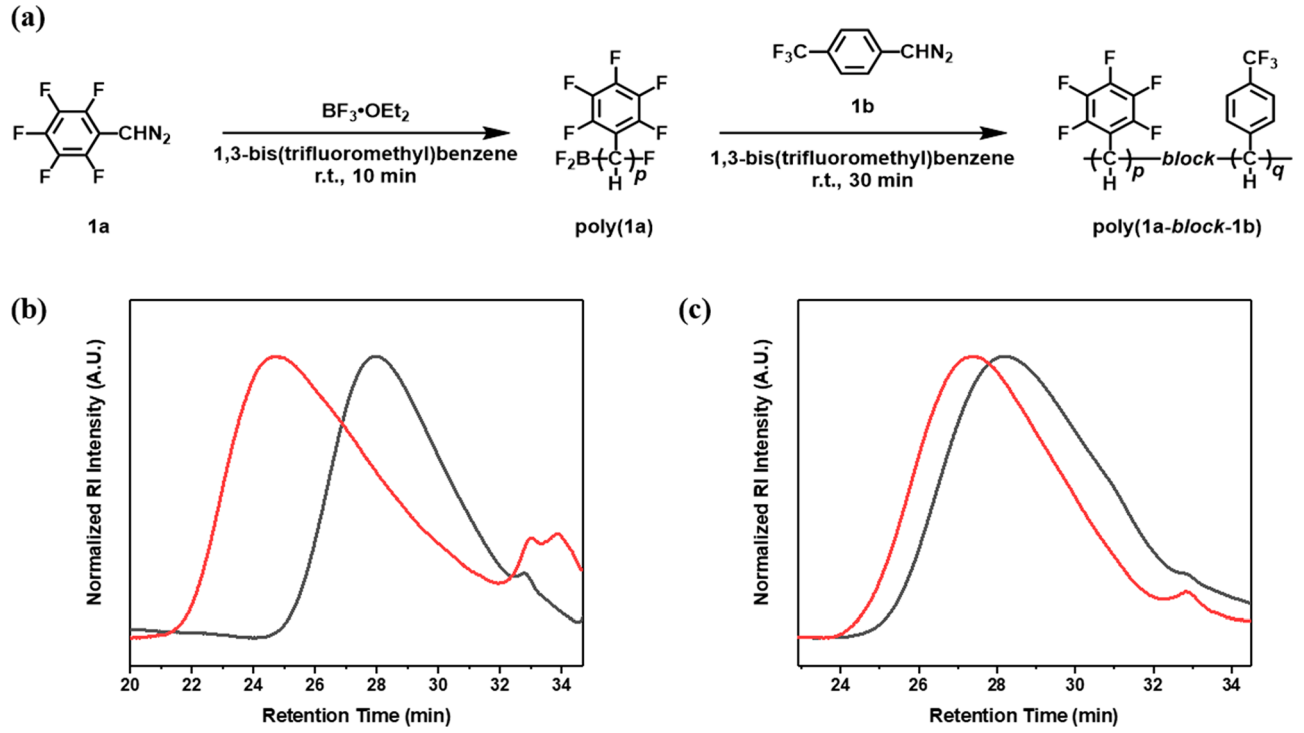

Figure 2. (a) Synthesis of a block copolymer of **1a** and **1b**. (bottom) (b) SEC data recorded for a homopolymer of **1a** before (black line; $[\mathbf{1a}]_0/[BF_3{\cdot}OEt_2]_0 = 25$; $M_n = 9.9$ kDa, $Đ = 1.09$) and after (red line; $([\mathbf{1a}]_0 + [\mathbf{1a}]_1)/[BF_3{\cdot}OEt_2]_0 = 75$; $M_n = 13.4$ kDa, $Đ = 1.16$) adding a second feed of **1a**. Conditions: $[\mathbf{1a}]_0 = 0.48$ M, $[\mathbf{1a}]_1 = 0.48$ M, 1,3-bis(trifluoromethyl)benzene, r.t. Isolated yield was 66%. (c) SEC data recorded for a homopolymer of **1a** (black line; $[\mathbf{1a}]_0/[BF_3{\cdot}OEt_2]_0 = 25$; $M_n = 8.6$ kDa, $Đ = 1.17$) and its corresponding block copolymer with **1b**, poly(**1a**-*block*-**1b**) (red line; $([\mathbf{1a}]_0 + [\mathbf{1b}]_0)/[BF_3{\cdot}OEt_2]_0 = 75$; $M_n = 10.8$ kDa, $Đ = 1.07$). Conditions: $[\mathbf{1a}]_0 = 0.48$ M, $[\mathbf{1b}]_0 = 0.48$ M, 1,3-bis(trifluoromethyl)benzene, r.t. Isolated yield was 65%.

$BF_3{\cdot}OEt_2$ ($[\mathbf{1a}]_0/[BF_3{\cdot}OEt_2]_0 = 25$), and the resulting mixture was stirred at room temperature for 10 min. An aliquot was then removed and analyzed by SEC ($M_n = 9.9$ kDa, $Đ = 1.09$). Additional monomer ($[\mathbf{1a}]_1/[BF_3{\cdot}OEt_2]_0 = 50$) was subsequently added to the residual solution, and the mixture was stirred for 30 min at room temperature. As depicted in Figure 2b, SEC revealed that the polymer product increased in molecular weight upon exposure to additional monomer while retaining a low $Đ$ value (1.16). A well-defined block copolymer of **1a** and **1b**, poly(**1a**-*block*-**1b**), was also prepared through successive monomer addition. As shown in Figure 2c, the molecular weight measured for a homopolymer of **1a** shifted toward a higher value upon the introduction of **1b** to the polymerization reaction mixture. Moreover, the copolymer exhibited new ^{1}H NMR signals at 7.02 and 2.99 ppm (hexafluorobenzene with C_6D_6; see Figure S84), which were assigned to the protons of the phenyl ring and the backbone of the homopolymer block of **1b**, respectively. The composition of the copolymer was determined and matched the monomer feed ratio (**1a**/**1b** = 1:2). A new ^{19}F NMR signal at −63.01 ppm, which was assigned to the trifluoromethyl group of the poly(**1b**) block was also observed while diagnostic signals at −134.10, −150.18, and −160.06 ppm (hexafluorobenzene) were in agreement with the signals previously recorded for poly(**1a**) (see Figure S86).[70]

Having verified that the polymerization of **1a** proceeded in a controlled, chain-growth fashion, subsequent efforts were directed toward exploring how the synthetic precision juxtaposed with the unique C1 polymer structure manifested as a hydrophobic material.[71] The degree of hydrophobicity was assessed in terms of wettability, which was quantified using a series of contact angle measurements.[72] A solution of poly(**1a**) in chloropentafluorobenzene ($[\text{poly}(\mathbf{1a})]_0 = 5$ mg mL^{-1}) was spin coated onto a silica wafer and then dried under vacuum. The water static contact angle and the contact angle hysteresis (CAH), defined as the difference between the advancing and receding contact angles,[73,74] of the film were measured to be 101.4° and 22.4°, respectively, and indicated that the polymer was highly hydrophobic.[75] For reference, a lower static contact angle (91.8°) and a higher CAH (48.7°) were measured for poly(phenyl methylene), the hydrogenated parent of poly(**1a**).

Next, efforts were directed toward comparing C1 polymers, such as poly(**1a**) and poly(phenyl methylene), to their C2 analogues, poly(styrene) (PS) and poly(2,3,4,5,6-pentafluorostyrene) (FPS). The C2 polymers were obtained from commercial sources or prepared using literature procedures.[21] As expected,[76] the static contact angle measured for FPS (95.8°) was more obtuse than the value measured for PS (89.8°) and a lower CAH value was measured for the former (c.f., 55.0° vs 71.7°). However, the C1 polymers appeared to be more hydrophobic than their C2 analogues. For example, the static contact angle measured for poly(phenyl methylene) (91.8°) was higher than that measured for PS (89.8°), and a more pronounced increase was observed when comparing poly(**1a**) to FPS (c.f., 101.4° vs 95.8°). Similar conclusions were drawn by analyzing the corresponding CAH data. The increased hydrophobic effects were attributed to the relatively high densities of the pendant groups found in the C1 polymers.

Once it was established that the C1 polymers were more hydrophobic than their C2 analogues, subsequent efforts were directed toward exploring if such properties could be tuned through structural variation. Thus, the other fluorinated

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Table 2. Summary of Data Recorded for Various Fluorinated and Hydrogenated Polymers[a]

entry	polymer	M_n (kDa)	$Đ$	static contact angle (°; H_2O)	static contact angle (°; CH_2I_2)	advancing contact angle (°; H_2O)	receding contact angle (°; H_2O)	contact angle hysteresis (°)
1	poly(**1a**)[b]	14.2[f]	1.14	101.4	66.0	105.1	82.7	22.4
2	poly(phenyl-methylene)[c]	6.0[g]	2.98	91.8	[h]	94.9	46.2	48.7
3	poly(2,3,4,5,6-pentafluorostyrene)[b]	8.1[g]	1.21	95.8	41.2	98.3	43.3	55.0
4	poly(styrene)[c]	9.22[f]	1.07	89.8	[h]	95.1	23.4	71.7
5	poly(**1b**)[b]	11.2[f]	1.12	97.0	63.4	103.0	77.2	25.8
6	poly(**1c**)[d]	4.2[g]	1.69	85.6	32.4	89.8	49.2	40.6
7	poly(**1d**)[b]	10.2[f]	1.19	91.8	48.1	93.2	58.7	34.5
8	poly(**1e**)[d]	11.3[g]	1.98	94.0	37.9	95.3	53.1	42.2
9	poly(**1f**)[c]	11.8[g]	1.25	94.3	46.3	94.9	43.2	51.7
10	poly(**1g**)[e]	11.1[f]	1.05	106.4	86.9	111.4	88.9	22.5

[a]Obtained using the sessile drop method at room temperature with water as the solvent. Thermal annealing at 80 °C for 3 h did not significantly alter the contact angle data. [b]A film was spin-coated onto a silica wafer using 5 mg mL^{-1} of the polymer solution in chloropentafluorobenzene. [c]A film was spin-coated onto a silica wafer using 5 mg mL^{-1} of the polymer solution in toluene. [d]A film was spin-coated onto a silica wafer using 5 mg mL^{-1} of the polymer solution in chloroform. [e]A film was spin-coated onto a silica wafer using 5 mg mL^{-1} of the polymer solution in hexafluorobenzene. [f]Measured using SEC with chloropentafluorobenzene as the solvent against poly(dimethylsiloxane) standards. [g]Measured using SEC with THF as the solvent against poly(styrene) standards. [h]No data were recorded due to a lack of solubility in diiodomethane.

monomers described in Scheme 2 were polymerized and then analyzed;[77] key results are summarized in Table 2.[78] Several trends were identified upon inspection of the data. First, hydrophobicity appeared to be strongly affected by the number of fluorine atoms in the pendant groups.[79] Poly(**1a**), which featured five fluorine atoms, exhibited the highest static contact angle (101.4°) followed by poly(**1b**) and poly(**1d**), which featured three and two fluorine groups, respectively. Second, the static contact angles measured for polymers that featured monosubstituted phenyl groups were found to be inversely proportional to the distance of the F group to the polymer backbone (c.f., *ortho*, 85.6°; *meta*, 91.8°; *para*, 94.0°). The result was attributed to the differences in the surface dipoles displayed by the corresponding polymers.[72] A combination of fluorine density and surface dipole were also found to affect the static contact angle. For example, poly(**1e**) features a lower density of fluorine atoms when compared to poly(**1c**) or poly(**1d**) but a relatively high static contact angle. Likewise, poly(**1b**) and poly(**1f**) feature the same number of fluorine atoms but the static contact angle measured for the former was relatively high (c.f., 97.0° vs 94.3°). In addition, based on these results, poly(**1g**), which features a pendant heptafluorotolyl substituent, was hypothesized to exhibit the most hydrophobic characteristics of the polymers tested as it features a relatively high density of fluorine groups and thus can be expected to be exhibit a high surface dipole. Indeed, a static contact angle of 106.4° was measured for a film prepared using the polymer. The measured value is comparable to that reported for PTFE (108−114°),[80] yet poly(**1g**) can be dissolved and processed like other thermoplastics, which underscores an intrinsic advantage. Similar contact angle trends were observed when diiodomethane was used in lieu of water, which indicated that solvent polarity did not negate the surface energies intrinsic to the polymers.

In summary, we have developed a method that transforms fluoro-containing aryl diazomethanes into novel fluorinated polymers. The polymerization of 2,3,4,5,6-pentafluorophenyl diazomethane effectively grows polymer chains in one carbon increments, provides control over polymer molecular weight and polydispersity, and offers access to relatively advanced derivatives, including block copolymers. Through a series of static and dynamic contact angle measurements, it was determined that the fluorinated polymers described herein are more hydrophobic than their C2 analogues. To the best of our knowledge, this is the first example of such a comparison and further illustrates the unique and beneficial properties afforded by the highly substituted polymers that are obtained from C1 polymerizations. Moreover, the methodology was expanded to include a series of fluoro-containing aryl diazomethanes and afforded access to processable derivatives that exhibited high hydrophobicities.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.1c00686.

General information, synthetic procedures, SEC data, thermal data, contact angle measurement data, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Christopher W. Bielawski − *Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea; Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea;* orcid.org/0000-0002-0520-1982; Email: bielawski@unist.ac.kr

Authors

Songsu Kang − *Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea*

Sherilyn J. Lu − *Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea; Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmacrolett.1c00686

Author Contributions

†S.K. and S.J.L. contributed equally to this work and should be considered as cofirst authors.

Notes

The authors declare no competing financial interest.

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(68) The SEC data suggested to us that only one polymer chain grew from each boron center. The result is in contrast to results that have been reported with trialkyl boron catalysts, which have been shown to grow three polymers from each boron center.[37] If there had been an equal probability of the polymerization occurring at all three B−F bonds, the expected M_n would have been one-third that of the theoretical value. The difference may be due to the strength of the B−F bond, which is higher than that of the B−C bond. Thus, after the initiation event, only one polymer chain appears to grow from the boron center.
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