# Multi-armed, TEMPO-functionalized unimolecular initiators for starburst dendrimer synthesis via stable free radical polymerization. 1. Tri azofunctionalized unimer

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**Abstract:** The synthesis of azobenzene-functionalized multi-armed unimolecular initiators or "*unimers*" that can be polymerized using styrene or styrenic derivatives via TEMPO (2,2,6,6-tetramethylpiperidenyl-1-oxyl) mediated stable free radical polymerization (SFRP) is described. The unimers are composed of an azobenzene-functionalized core and a TEMPO-modified unit. Homopolymers and copolymers of styrene and acetoxystyrene were synthesized using the mono-and trifunctionalized unimers as initiators under bulk conditions with average molecular weights and polydispersities reported. The studies lay the groundwork for further investigations involving SFRP towards building a light harvesting system by introducing chromophores onto the polymer chains for capturing light and thence transferring it to the azobenzene core.

Key words: azo-functionalized unimolecular initiator, stable free radical polymerization, starburst dendrimer.

**Résumé :** On décrit la synthèse d'initiateurs unimoléculaires tentaculaires à base d'azobenzènes, dénommés unimères, qui peuvent être polymérisés à l'aide de styrène ou de ses dérivés par le biais d'une polymérisation avec un radical libre stable catalysée par le 2,2,6,6-tétraméthylpipéridinyl-1-oxyle (TEMPO). Les unimères sont formés d'un noyau azobenzène fonctionnalisé et d'une unité TEMPO modifiée. On a synthétisé des homopolymères et des copolymères du styrène et de l'acétoxystyrène en utilisant des unimères mono- et trifonctionnalisés comme initiateurs, dans des conditions globales, et on rapporte des poids moléculaires et des polydispersités moyennes. Les études posent les fondements pour des études ultérieures, impliquant des polymérisations avec un radical libre stable, dans l'élaboration d'un système permettant de recueillir la lumière en introduisant sur les chaînes de polymère des chromophores qui pourraient capter la lumière et par la suite la transmettre au noyau azobenzène.

*Mots clés :* initiateur unimoléculaire à base d'azobenzène fonctionnalisé, polymérisation avec un radical libre stable, dendrimère en « éclatement d'étoile ».

[Traduit par la Rédaction]

## Introduction

The synthesis of macromolecules with "complex" and controlled architecture is becoming increasingly important in the field of polymer chemistry (1). There are two categories of complexity that one can introduce: functional complexity and architectural complexity. Azo moieties are an example of functional complexity since they can operate as optical transducers, i.e., through light absorption, energy transfer, and cis/trans isomerism. The second category, architectural complexity, can be achieved by introducing branches into the polymer backbone, which leads to the formation of graft or star polymer systems. In our study, we would like to couple these two categories of complexity in a single system to enable the investigation of the unique properties of this system.

Traditional methods of synthesizing well-defined macromolecular architectures involve *living* polymerization techniques such as anionic (2), cationic (3), group transfer polymerization (4), and transition-metal catalysis (5). However, as a result of work over the past decade living free radical polymerization is now possible where there is control over the molecular weight, the end group, and the ability to synthesize block copolymers.

Georges et al. (6) were the first to report the synthesis of low polydispersity polystyrene using free radical polymer-

Received 2 February 2004. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 9 November 2004.

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Scheme 1.



ization, based on use of the stable nitroxide radical 2,2,6,6tatramethylpiperdinyloxy (TEMPO) in combination with benzoyl peroxide (BPO) as a *bimolecular* initiating system. The TEMPO unit acts as a "capping" agent for the growing polymer chain and controls the polymerization (7). The use of stable nitroxides to control free radical polymerization was originally stimulated by the work of Moad and Rizzardo (8) who employed TEMPO to reversibly terminate a growing polymer chain.



During the past decade much work has been done on designing and synthesizing functionalized *unimolecular* initiators that contain the TEMPO unit. Some examples of unimolecular initiators synthesized by Hawker and coworkers (9, 10) are shown below. Compounds **1**, **2**, **3**, and **4** are *monofunctionalized* unimolecular initiators that form linear polymers upon polymerization, while compound **5** is a *trifunctionalized* unimolecular initiator that forms a star polymer upon polymerization, where T stands for the TEMPO moiety.



The work described in this paper focuses on the synthesis of *multiazofunctionalized* azo unimolecular initiators, which we call "unimers", for stable free radical polymerization (SFRP). The structures of the unimers are shown below, where 6 and 7 are used in the synthesis of 8, 9, and 10, i.e., monoazofunctionalized, diazofunctionalized, and triazofunctionalized unimers, respectively. The mono- and trifunctionalized unimers were used in the polymerization of styrene and acetoxystyrene to form homopolymers, block copolymers, and random copolymers, where we report the average molecular weights and polydispersities based on GPC analysis.

We are specifically interested in azobenzene-modified polymers to study and compare cis/trans isomerization of the azobenzene units of the mono-, di-, and trifunctionalized polymers upon irradiation. It is anticipated that cis/trans isomerism of the azo core should have a profound effect on the overall tertiary structure of the molecules.

The present work continues our studies with azo, azoxy, and hydrazo arenes, encompassing various structure reactivity studies, such as rearrangements (Wallach, benzidine), spiropyran-merocyanine interconversion systems, and periphery-modified dendrimers, with applications in optical data storage, holography and drug delivery, as well as light harvesting properties (11).

## **Results and discussion**

Our strategy is to develop the chemistry on a monoazofunctionalized unimer 8 and then extend this chemistry to the more complex difunctionalized 9 and trifunctionalized **GEN 0** unimer systems.

#### Monoazofunctionalized unimolecular initiator 8

The monoazofunctionalized unimer **8** is composed of two parts, the core, *p*-hydroxyazobenzene **14** and the TEMPO-containing unit, TEMPO modified 4-ethylbenzyl iodide **7**. Scheme 1 shows the preparation of TEMPO-modified 4-ethylbenzyl iodide **7** starting from commercially available 4-ethylbenzaldehyde **11**.

To introduce a TEMPO unit and form the TEMPOmodified derivative of compound **13**, a carbon-centered radical must be generated in the presence of TEMPO. Hawker et al. (9) used di-*tert*-butyl peroxide to generate the carbon-







centered radicals at ca. 125 °C. We used di-*tert*-butyl peroxyoxalate instead since it undergoes facile decomposition in solvents such as benzene below 50 °C to give *tert*-butoxy radicals.

Coupling of the azobenzene core with the TEMPOcontaining unit was first attempted using the bromo derivative **6** with poor yield (9%) (12). To optimize the yield, the iodo derivative **7** was synthesized using the Finkelstein reaction.

The monofunctionalized azobenzene unimer was synthesized as shown in Scheme 1 in 75% yield (16). The proton NMR spectrum confirms that the azobenzene core became attached to the TEMPO-containing unit. The aromatic protons on the azobenzene unit appear at 7 to 8 ppm and the TEMPO unit protons at 0.5–0.6 ppm.

#### Diazofunctionalized unimolecular initiator 9

The difunctionalized azobenzene unimer 9 is composed of a core containing two azobenzene units and two TEMPOmodified units attached to the ends of the core. The synthesis of 9 was accomplished in 62% yield as shown in Scheme 2.

Coupling of the TEMPO units onto bis(4-aminophenyl)-1,2-ethane **16** to form the difunctionalized azobenzenemodified unimer was effected by reaction with **7** (Scheme 1) (18% yield).

#### Triazofunctionalized unimolecular initiator 10, GEN 0

The trifunctionalized unimer is the zeroth generation of a dendrimer, i.e., **GEN 0**, a star-shaped unimer composed of a

Scheme 2.



core with three azobenzene units and three TEMPOmodified units attached to the ends of the core.

The preparation of **GEN 0** (Scheme 3) involved first the synthesis of the core 21 in three steps:

- (1) Nucleophilic aromatic substitution yielded **19**.
- (2) Reduction of 19 gave 20 in 94% yield.
- (3) Diazotization and coupling gave **21** in 73% yield.

Introduction of the TEMPO units to form **GEN 0** was effected by Williamson ether coupling between the azobenzene core and the TEMPO-modified 4-ethylbenzyl iodide 7 (Scheme 1) in 22% yield (12). **Gen 0** is readily soluble in halogenated solvents such as dichloromethane or chloroform, and can be distinguished from the starting compound **21**, which dissolves only in acetone or DMSO. <sup>1</sup>H NMR shows the TEMPO moiety between 0.7 and 1.7 ppm and the aromatic protons between 7 and 8 ppm.

### Controlled free radical polymerizations

We now describe polymerization studies that have been performed towards synthesis of polymers having an azobenzene unit at the core. The studies entailed the mono- and trifunctionalized azobenzene unimers that were used in the polymerization of styrene and acetoxystyrene, to give homopolymers, block and random copolymers.

### Controlled free radical polymerization of monoazofunctionalized unimer

### Monoazo-functionalized polystyrene MAz-PS-T

Polymerization of styrene with monofunctionalized azobenzene unimer **8** was effected under bulk conditions (Scheme 4) at 135 °C. The polymerization was stopped after 2 h by cooling to room temperature. The polymer **MAz-PS-T** was dissolved in THF and precipitated from methanol to give a yellow powder (26%) with an average molecular weight of 13 500 g/mol and a narrow polydispersity of 1.26 Scheme 4.



based on GPC analysis. The <sup>1</sup>H NMR shows broad peaks at 1.4 and 1.8 ppm representing the aliphatic hydrogens of the polystyrene, the methylene and methine protons, respectively. Aromatic hydrogens of polystyrene appear as broad peaks between 6.4 and 7.2 ppm. The <sup>13</sup>C NMR shows a peak at 145.6 ppm for the quaternary carbon of the aromatic moiety of polystyrene while the other carbons of the aromatic moiety appear at 128.4, 128.1, and 126.1 ppm. Aliphatic carbons appear at 44.3 and 40.7 ppm. The UV–vis absorption spectrum of **MAz-PS-T** in THF showed distinct  $\pi$ – $\pi$ \* and n– $\pi$ \* absorption bands of azobenzene appearing at ca. 350 and 450 nm, respectively, confirming that the polymer sample contains the azobenzene unit.

#### Monoazofunctionalized polyacetoxystyrene MAz-PAS-T

The polymerization of acetoxystyrene with **8** was effected under the same conditions as for **MAz-PS-T**, in bulk, under nitrogen and heating at 135 °C as illustrated in Scheme 5. The polymerization was stopped after 75 min at which point the mixture became too viscous for stirring. A yellow powder (**MAz-PAS-T**) with an average molecular weight of 35 300 g/mol and a polydispersity of 1.34 formed upon dissolving the reaction mixture in THF and precipitating from methanol (49%). The <sup>1</sup>H NMR shows two broad peaks between 1.2 and 2.0 ppm representing the aliphatic protons of polyacetoxystyrene and a broad peak between 6.2 and 6.9 ppm for the aromatic protons of polyacetoxystyrene. The

methyl protons of the acetoxy group appear as a singlet at 2.3 ppm. The <sup>13</sup>C NMR shows a peak at 169.5 ppm representing the carbonyl carbon of the acetate group. Peaks at 149.1 and 142.6 ppm represent the quaternary carbons of the aromatic moiety of the polyacetoxystyrene while peaks at 128.8, 127.6, 122.0, and 121.5 represent the rest of the aromatic carbons. Aliphatic carbons of polyacetoxystyrene appear at 44.1 and 40.5 ppm representing the methylene and methine protons, respectively. The methyl carbon of the acetate group appears at 21.6 ppm.

### Monoazofunctionalized block (acetoxystyrene-styrene) copolymer MAz-PAS-PS-T

Chain extension of **MAz-PAS-T** with styrene under bulk conditions yielded **MAz-PAS-PS-T**, a block copolymer of acetoxystyrene and styrene, as illustrated in Scheme 6. The polymerization was stopped after 2 h and the reaction mixture was dissolved in THF and precipitated from methanol to give an off-white – yellow powder with an average molecular weight of 40 400 g/mol and 1.54 polydispersity. The <sup>1</sup>H NMR shows the aliphatic protons of the polymer chain between 1.2 and 2.2 ppm and the aromatic protons between 6.2 and 7.5 ppm. The methyl protons of the acetate group appear as a singlet at 2.3 ppm. The <sup>13</sup>C NMR shows the carbonyl carbon of the acetate group at 169.5 ppm, the quaternary aromatic carbons of the polyacetoxystyrene at 149.1 and 142.6 ppm and the quaternary aromatic carbon of polystyScheme 7.



rene at 145.7 ppm. The rest of the aromatic carbons of the polymer chain appear at 128.4, 128.1, 126.0, and 121.5 ppm. The aliphatic carbons appear at 46.2, 44.0, 43.2, and 40.8 ppm. The methyl carbon of the acetoxy group appears at 21.6 ppm consistent with the block copolymer structure.

#### Monoazofunctionalized random (acetoxystyrene-styrene) copolymer MAz-PAS/PS-T

Contrasting with the design for block copolymer MAz-PAS-PS-T, where the strategy is to begin with polymer MAz-PAS-T and under SFRP react that with acetoxystyrene, the second monomer was reacted simultaneously to give a random copolymer.

Thus, polymerization of acetoxystyrene, styrene (1:2 volume ratio), and monofunctionalized azobenzene unimer **8** under bulk conditions yielded the random copolymer **MAz-PAS/PS-T** as shown in Scheme 7. The polymer was dissolved in THF and precipitated from methanol, filtered and dried to give a yellow solid with an average molecular weight of 16 400 g/mol and a polydispersity of 1.24.

#### Monoazofunctionalized poly(4-hydroxystyrene) MAz-PHS-T

The hydrolysis of **MAz-PAS-T** was effected by adding ammonium hydroxide to a solution of **MAz-PAS-T** in methanol under reflux conditions as shown in Scheme 8. The polymer was precipitated from water, filtered and dried to give yellow crystals in 40% yield. The absence of a <sup>13</sup>C carbonyl peak at 165.9 ppm confirms that the hydrolysis is complete. The aromatic quaternary carbon attached directly to the hydroxy group appears at 155.3 ppm while the other aromatic quaternary carbon appears at 137.0 ppm. The other aromatic carbons of the polymer chain appear at 128.8 and 115.1 ppm. Aliphatic carbons of the polymer chain appear between 28.6 and 39.7 ppm.

### Controlled free radical polymerization of a triazofunctionalized unimer

#### Polyacetoxystyrene starburst azo dendrimer TAz-PAS-3T

Polymerization of acetoxystyrene with triazofunctionalized unimer GEN 0 was done under bulk conditions by heating the reaction mixture at 135 °C as illustrated in Scheme 9. The polymerization was stopped after 75 min. The polymer was dissolved in THF and precipitated from methanol, filtered and dried to give a yellow powder (**TAz-PAS-3T**) a star polymer, with an average molecular weight of 74 400 g/mol and a polydispersity of 1.49 based on light scattering detector analysis.

### Starburst block (acetoxystyrene-styrene) azo dendrimer TAz-PAS-PS-3T

The block copolymer **TAz-PAS-PS-3T** was synthesized by polymerizing **TAz-PAS-3T** with styrene under bulk conditions at 135 °C, as shown in Scheme 10. The polymerization was stopped after 45 min and the reaction mixture was dissolved in THF and precipitated from methanol, filtered and dried to give an off-white – yellow solid with an average molecular weight of 126 000 g/mol and a polydispersity of 1.64 based on light scattering detector analysis.

#### Conclusions

In conclusion, it has been shown in this work that functionally and architecturally dendritic structures with azo cores can be synthesized using controlled radical polymerization.

The synthesis of mono-, di-, and triazofunctionalized unimers was accomplished by coupling of the azobenzene cores, **14**, **16**, and **21**, with TEMPO-modified 4-ethylbenzene **7**. A combination of <sup>1</sup>H and <sup>13</sup>C NMR and mass spectra was used for full characterization of the unimers.

The mono- and trifunctionalized unimers were used in polymerization reactions with styrene and acetoxystyrene. Structures of the azobenzene-modified polymers were characterized by means of a combination of <sup>1</sup>H and <sup>13</sup>C NMR and UV–vis spectra. The monoazofunctionalized unimer **8** was polymerized with styrene to form a homopolymer, **MAz-PS-T**, with  $M_n$  value 13 500 and PD 1.26. Polymerization with acetoxystyrene yielded a polymer, **MAz-PAS-T**, with  $M_n$  35 300 and PD 1.34. Copolymers of styrene and acetoxystyrene were also synthesized, where a block copolymer, **MAz-PAS-PS-T**, with  $M_n$  40 400 and a PD 1.54 and a

#### Scheme 9.



Scheme 10.



random copolymer, MAz-PAS/PS-T, with  $M_n$  16 400 and PD 1.24 were obtained.

The trifunctionalized unimer, **GEN 0**, was also polymerized with acetoxystyrene to yield a polymer, **TAz-PAS-3T**, with  $M_n$  74 400 and PD 1.49. This polymer was copolymerized with styrene to give a block copolymer, **TAz-PAS-PS-3T**, with an  $M_n$  value of 126 000 and a PD of 1.64.

It is anticipated that the present polymers would have to be modified at the periphery to achieve light harvesting properties by functionalization with naphthyl moieties. The studies predict the formation of an *on/off* molecular switch through trans to cis isomerization of the azobenzene unit by irradiation of the naphthyl moieties and then energy transfer to the azo core.

## **Experimental section**

IR spectra were recorded on a Bomen MB-120 spectrophotometer as KBr disks.  $^{1}$ H and  $^{13}$ C NMR spectra were recorded on Bruker AM300 spectrophotometer (<sup>1</sup>H 300.1 MHz, <sup>13</sup>C 75.5 MHz). Chemical shifts are reported in parts per million (ppm) relative to the peaks for residual CHCl<sub>3</sub> in CDCl<sub>3</sub> ( $\delta$  7.28 ppm) and acetone- $d_5$ H in acetone- $d_6$  ( $\delta$  2.05 ppm). Mass spectrometry results were recorded on a Fisons VG Quattro (triple-quadropole MS–MS). Several techniques were used to identify the mass of the parent ion, such as electron ionization (EI), chemical ionization (CI), fast atom bombardment (FAB), and electrospray (ES). High-resolution mass spectrometry (HR-MS) to establish molecular weights of new compounds was performed by the University of Ottawa Mass Spectrometry Service and University of Alberta Mass Spectrometry Service. Melting points were determined on a Mel-Temp capillary melting point apparatus and were not corrected.

#### 4-Ethylbenzyl alcohol 12 (13)

12 was prepared by reduction of 11 as outlined in Scheme 1. To a stirred solution of 11 (13.1 g, 97.8 mmol) in methanol (100 mL) was added a solution of sodium borohydride (1.4 g, 37.0 mmol) in sodium hydroxide (2 mL, 2 mol/L) and water (18 mL) dropwise while maintaining the temperature at 23 °C. After removing the solvent on a rotary evaporator, the residue was dissolved in water (200 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 mL). Drying (MgSO<sub>4</sub>), filtration, and solvent removal on a rotary evaporator followed by column chromatography using hexanes – ethyl acetate (2:1) as the eluant yielded **12** as a pale yellow oil (10.0 g, 82%). IR (KBr disk, cm<sup>-1</sup>): 3340, 2969, 2933, 2868, 1417, 1032, 813. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.28 (4H, dd), 4.61 (2H, s), 1.06 (1H, d), 2.73 (2H, q), 1.33 (3H, t). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 143.34, 138.03, 127.75, 127.00, 64.57, 28.39, 15.48.

### 4-Ethylbenzyl bromide 13 (12)

Triphenyl phosphine (11.8 g, 45.0 mmol) was added in two parts to a mixture of **12** (5.0 g, 36.8 mmol) and  $CBr_4$ (14.8 g, 44.6 mmol) in dry THF (75 mL) and stirred under argon for 2 h. After removing the solvent by rotary evaporation, the residue was dissolved in water (100 mL) and extracted with  $CH_2Cl_2$  (3 × 50 mL), dried over MgSO<sub>4</sub>, filtered, and the solvent was evaporated on a rotary evaporator. Column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluant yielded a pale yellow oil (7.0 g, 95%). IR (KBr disk, cm<sup>-1</sup>): 3062, 2962, 2926, 2868, 1898, 1618, 1510, 1438, 1222, 827. <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 7.40, 7.26 (4H, dd), 4.58 (2H, s), 2.74 (2H, q), 1.34 (3H, t). <sup>13</sup>C NMR (CDCl<sub>3</sub>) & 144.72, 135.08, 129.11, 128.36, 33.81, 28.66, 15.49. EI-MS *m/z*: 198.4 and 199.9 (calcd. for C<sub>9</sub>H<sub>11</sub>Br: 198.0 and 200.0).

### Di-tert-butylperoxyoxalate (14)

A solution of oxalyl chloride (2.5 mL) in petroleum ether (25 mL) was added slowly to a stirred cold solution of anhydrous pyridine (4 mL) and 5.5 mol/L solution of *tert*-butyl hydroperoxide (5 mL) in petroleum ether (50 mL) over 20 min while maintaining the temperature at -4 °C. The reaction mixture was then warmed to 15 °C where the white precipitate formed was filtered and the filtrate was cooled for 15 min in dry ice – acetone (-78 °C) to allow crystallization of peroxyoxalate as fine white crystals. The solvent was decanted and the peroxyoxalate crystals, 4.01 g (69%), dried under argon and stored in the refrigerator.

#### **TEMPO-modified 4-ethylbenzyl bromide 6 (15)**

As outlined in Scheme 1, a mixture of 13 (5 g, 25.1 mmol), TEMPO (3 g, 19.2 mmol) and di-tert-butylperoxyoxalate (4 g, 1.59 mmol) in benzene (40 mL) was stirred and heated to 35 °C under argon for 24 h. After removing the solvent by rotary evaporation the product was purified by column chromatography using hexanes-dichloromethane (1:1) as the eluant to give the TEMPO modified 4ethylbenzyl bromide 6 as a white solid (1.78 g, 20%), mp 63 to 64 °C. IR (KBr disk, cm<sup>-1</sup>): 3013, 2969, 1509, 1442, 1227, 1056, 842, 697. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.36 (4H, dd), 4.80 (1H, q), 4.52 (2H, s), 1.50 (3H, d), 1.41-1.11 (6H, m), 1.31, 1.27, 1.09, 1.05 (18H, each br s). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 146.20, 136.17, 128.79, 126.98, 82.71, 59.69, 40.35, 34.19, 33.72, 23.51, 20.36, 17.22. CI-MS m/z: 354.144 548 and 356.141 660 (1:1) (calcd. for C<sub>18</sub>H<sub>28</sub>NOBr: 353.135 41 and 355.133 54).

#### TEMPO-modified 4-ethylbenzyl iodide 7 (16)

Following the Finkelstein reaction outlined in Scheme 1, 6 (0.90 g, 2.91 mmol) was added to a stirred solution of sodium iodide (7.5 g, 50 mmol) in dry acetone (20 mL), which was refluxed under argon for 3 h. After filtering and removal of the solvent by rotary evaporation, the solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and extracted with water (50 mL) and  $CH_2Cl_2$  (2 × 50 mL) where the extracts were dried over MgSO<sub>4</sub>, filtered and the solvent evaporated to yield a white solid (7) (1.1 g, 94%), mp 72 °C. IR (KBr disk, cm<sup>-1</sup>): 3004, 2922, 1506, 1446, 1280, 1055, 874, 836, 699. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.36, 7.27 (4H, dd,), 4.77 (1H, q), 4.49 (2H, s), 1.61-1.18 (6H, m), 1.47 (3H, d), 1.23, 1.18, 1.04, 0.68 (12H, each br s). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 145.51, 137.51, 128.35, 126.92, 82.55, 59.57, 40.23, 34.33, 23.26, 20.30, 17.10, 5.96. CI-MS m/z: 402.131 155 (calcd. for C<sub>18</sub>H<sub>28</sub>NOI: 401.121 6).

#### Monoazofunctionalized unimer 8 (12)

**8** was synthesized by the coupling of **7** and *para*-hydroxyazobenzene **14** as illustrated in Scheme 1. A mixture

of 7 (1.0 g, 2.49 mmol), 14 (0.60 g, 3.03 mmol), anhyd. K<sub>2</sub>CO<sub>3</sub> (0.54 g, 3.91 mmol), and crown ether (0.24 g, 0.91 mmol) in dry acetone (50 mL) was refluxed (60 °C) under argon for 48 h. After removal of the solvent by rotary evaporation, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and extracted with water  $(3 \times 50 \text{ mL})$ . The organic layer was dried over MgSO<sub>4</sub>, filtered, and the solvent was removed by rotary evaporation. Column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluant yielded an orange solid 7 (0.75 g, 75%), mp 125 to 126 °C. IR (KBr disk, cm<sup>-1</sup>): 3064, 2968, 1497, 1457, 1251, 1145, 930, 836, 687. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.94 (2H, d), 7.90 (2H, d), 7.55–7.32 (3H, m), 7.40 (4H, d), 7.12 (2H, d), 5.16 (2H, s), 4.83 (1H, q), 1.51 (3H, d), 1.58-1.26 (6H, m), 1.26, 1.19, 1.06, 0.70 (12H, each br s). <sup>13</sup>C NMR (CDCl<sub>3</sub>) & 160.10, 158.30, 145.92, 130.77, 129.44, 127.75, 127.29, 125.14, 122.97, 115.53, 83.21, 70.70, 59.97, 40.76, 30.83, 23.60, 20.44, 17.26. CI-MS m/z: 472.294 317 (calcd. for C<sub>30</sub>H<sub>37</sub>N<sub>3</sub>O<sub>2</sub>: 471.2885).

#### Diazofunctionalized core 16 (16)

16 was synthesized from 4,4'-ethylenedianiline 15 via diazotization and coupling as shown in Scheme 2. The diazonium salt solution resulting when a solution of stirred sodium nitrite (4.16 g, 60.3 mmol) in water (5 mL) was added slowly to a solution of 15 (5.0 g, 23.6 mmol) in aq. HCl (17 mL of HCl in 5 mL of water) cooled below 2 °C in an ice-water bath, was coupled with phenol as follows. The diazonium salt solution was added slowly with stirring to a solution of phenol (5.6 g, 59.6 mmol) in 10% sodium hydroxide (12.8 g NaOH in 120 mL water) while maintaining the reaction temperature below 2 °C and was allowed to stand in an ice-water bath for 1 h with stirring. After the solution was acidified slowly with concd. HCl, the resultant precipitate was filtered, washed with cold water several times, recrystalized from ethanol, and precipitated with ice to give a diazofunctionalized core 16 as a light orange solid (6.2 g, 62%), mp 245 to 246 °C. <sup>1</sup>H NMR (acetone- $d_6$ )  $\delta$ : (0.2 g, 0276), mp 245 to 246 c. If With (action  $a_6$ ) c. 9.10 (2H, s), 7.84 (4H, d), 7.79 (4H, d), 7.41 (4H, d), 7.01 (4H, d), 3.08 (4H, s). <sup>13</sup>C NMR (action  $a_6$ )  $\delta$ : 37.60, 116.14, 122.73, 125.09, 129.72. EI-MS m/z: 422.174 20 (calcd. for C<sub>26</sub>H<sub>22</sub>N<sub>4</sub>O2 422.174 28).

#### **Diazofunctionalized unimer 9 (12)**

9 was synthesized by the coupling of 7 with 16 as illustrated in Scheme 2. A mixture of 7 (0.50 g, 1.41 mmol), diazofunctionalized core 16 (0.24 g, 0.57 mmol), anhyd. K<sub>2</sub>CO<sub>3</sub> (0.040 g, 0.30 mmol), and crown-ether (0.030 g, 0.11 mmol) in dry acetone (20 mL) was refluxed (60 °C) under argon for 48 h. After removal of solvent by rotary evaporation, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and extracted with water (3  $\times$  50 mL), dried over MgSO<sub>4</sub>, filtered, and the solvent was removed by rotary evaporation. Column chromatography using hexanes - ethyl acetate (3:2) as the eluent yielded an orange solid 9 (0.1 g, 18%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.90 (4H, d), 7.80 (4H, d), 7.38 (8H, d), 7.29 (4H, d), 7.09 (4H, d), 5.13 (4H, s), 4.82 (2H, q), 3.04 (4H, s), 1.48 (6H, d), 1.60-0.60 (12H, m), 1.29, 1.18, 1.03, 0.68 (24H, each br s). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 124.47, 122.49, 127.59, 126.87, 126.87, 114.88, 82.67, 69.74, 37.39, 23.38, 34.06, 29.51, 28.44, 20.77, 20.23, 20.20. EI-MS m/z: 969.600 22 (calcd. for C<sub>62</sub>H<sub>76</sub>N<sub>6</sub>O4: 969.600 08).

### 1,3,5-Tris(4'-nitrophenoxy)benzene 19 (17)

1,3,5-Tris(4'-nitrophenoxy)benzene was prepared via S<sub>N</sub>Ar displacement as outlined in Scheme 3. A mixture of 1,3,5trihydroxybenzene dihydrate (phloroglucinol) 17 (12.40 g, 76.50 mmol), 4-fluoronitrobenzene 18 (24.4 mL, 230 mmol), potassium fluoride (26.70 g, 460.0 mmol), and 150 mL of DMSO was heated to reflux temperature for 30 min. The reaction mixture was then cooled to room temperature (r.t.), and the precipitate was filtered, washed with water (150 mL), and allowed to dry to give a crude product as a tan flaky solid, which was recrystallized from ethyl acetate - charcoal and followed by chloroform-hexanes to give 1,3,5-tris(4'-nitrophenoxy)benzene 19 as a creamy white solid (25.0 g, 50%), mp 203 to 204 °C (lit. value (7) 203.5-205.5 °C). IR (KBr disk, cm<sup>-1</sup>): 3091, 2840, 2448, 1918, 1591, 1561, 1468, 1340, 1230, 1114, 994, 848, 741, 632. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 8.27 (6H, d), 7.15 (6H, d), 6.67 (3H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 161.30, 157.77, 143.60, 126.09, 118.21, 107.60. EI-MS m/z: 489.0819 (calcd. for C<sub>24</sub>H<sub>15</sub>N<sub>3</sub>O9 489.080 1).

#### 1,3,5-Tris(4'-aminophenoxy)benzene 20 (18)

The synthesis of 20 is outlined in Scheme 3. To a stirred solution of 19 (8.0 g, 16 mmol) and Fe powder (8.10 g, 145 mmol) in 50% ethanol (100 mL) was added slowly HCl (0.6 mL concd. HCl in 10 mL of 50% ethanol) and the reaction mixture was refluxed for 2 h. After the reaction mixture was made alkaline by addition of 15% KOH, the iron was filtered quickly and washed with 95% ethanol ( $2 \times 50$  mL). The solvent was removed by rotary evaporation and the residue was dissolved in chloroform (100 mL) and extracted with water  $(3 \times 500 \text{ mL})$ . The organic layer was dried over MgSO<sub>4</sub>, filtered, and the solvent was evaporated on a rotary evaporator. The residue was dried under vacuum for 48 h to give 1,3,5-tris(4'-aminophenoxy)benzene 20 as a light purple solid (6.10 g, 94%), mp 88-90 °C (lit. value (8) 88 to 89 °C). IR (KBr disk, cm<sup>-1</sup>): 3424, 3352, 3212, 1606, 1503, 1451, 1214, 1113, 1003, 8.31. <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 6.86 (6H, d), 6.65 (6H, d), 6.18 (3H, s), 3.67 (6H, br s). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 160.77, 147.84, 142.90, 121.23, 116.17, 99.97. EI-MS *m/z*: 399.157 3 (calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O3 399.158 4).

#### Triazofunctionalized core 21 (13)

The trifunctionalized core 21 was synthesized from 20 via diazotization and coupling as illustrated in Scheme 3. A diazonium salt solution resulted when sodium nitrite (1.56 g, 22.6 mmol) in water (12 mL) was added slowly with stirring to a solution of 20 (3 g, 7.52 mmol) in aq. HCl (5 mL of HCl in 12 mL of water) cooled below 2 °C in an ice-water bath. The diazonium salt was added slowly with stirring to phenol (2.1 g, 22.3 mmol) in 10% sodium hydroxide (48 mL) while maintaining the reaction temperature below 2 °C and was allowed to stand in an ice-water bath for 1 h with stirring. After the solution was acidified with HCl the resultant precipitate was filtered, washed with cold water several times, and air-dried for a few days to give the trifunctionalized azobenzene core (21) as a dark red solid (4.50 g, 84%), mp 190 °C. IR (KBr disk, cm<sup>-1</sup>): 3405, 3168, 1451, 1312, 1225, 1146, 999, 685. 638. <sup>1</sup>H NMR (acetone*d*<sub>6</sub>) δ: 7.89 (6H, d), 7.81 (6H, d), 7.24 (6H, d), 6.99 (6H, d), 6.63 (3H, br s), 6.62 (3H, s). <sup>13</sup>C NMR (acetone- $d_6$ )  $\delta$ : 160.85, 159.55, 158.52, 149.35, 146.54, 125.17, 124.60, 119.72, 116.10, 105.45. EI-MS: 714.222 683 (calcd. for  $C_{42}H_{31}N_6O6$  714.222 7).

### Triazofunctionalized unimer 10 (GEN 0) (12)

GEN 0 was synthesized by coupling of 7 with 21 as illustrated in Scheme 3. A mixture of 7 (0.15 g, 0.37 mmol), the azo core 21 (0.11 g, 0.15 mmol), and anhyd.  $K_2CO_3$ (0.050 g, 0.58 mmol) in dry acetone (20 mL) was heated at reflux (60 °C) under argon for 48 h. After removal of the solvent by rotary evaporation, the residue was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as the eluant to give GEN 0 (0.05 g, 22%) as an orange thick oil. IR (KBr disk, cm<sup>-1</sup>): 2968, 2926, 2868, 2362, 2335, 1584, 1496, 1455, 1370, 1225, 1095, 1005, 838. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.91 (12H, d), 7.40 (12H, d), 7.18 (12H, d), 7.10 (2H, d), 6.58 (3H, s), 5.15 (6H, s), 4.84 (3H, apparent d), 1.51 (9H, d), 1.66-1.00 (18H, m), 1.32, 1.20, 1.07, 0.71 (36H, each br s). <sup>13</sup>C NMR (CDCl<sub>3</sub>) & 161.28, 159.07, 158.13, 149.12, 145.95, 134.85, 127.39, 126.93, 124.69, 124.47, 119.33, 115.18, 105.09, 82.86, 70.34, 59.76, 40.41, 34.50, 23.64, 20.37, 17.28. ES-MS: (M + H)<sup>+</sup> 1535.2 (calcd. for C<sub>96</sub>H<sub>111</sub>N<sub>9</sub>O9 1533.85).

# Polymerization of styrene with monoazofunctionalized unimer (MAz-PS-T)

**MAz-PS-T** was synthesized by polymerizing styrene with **8** under bulk conditions as illustrated in Scheme 4. A mixture of monofunctionalized unimer **8** (0.10 g, 0.20 mmol) and styrene (18.2 g, 17 5mmol) was heated at 135 °C under nitrogen for 3 h. The polymerization mixture was dissolved in 50 mL of THF and precipitated from 750 mL of methanol, filtered and dried in a vacuum oven at 70 °C resulting in a yellow powder (4.69 g, 26%).  $M_n = 13500$ ,  $M_w/M_n = 1.26$ .

## Polymerization of acetoxystyrene with monoazofunctionalized unimer (MAz-PAS-T)

**MAz-PAS-T** was synthesized by polymerizing acetoxystyrene with **8** under bulk conditions as illustrated in Scheme 5. A mixture of monofunctionalized unimer **8** (0.10 g, 0.20 mmol) and acetoxystyrene (26.6 g, 164 mmol) was heated at 135 °C under nitrogen for 75 min. The polymerization mixture was dissolved in 50 mL of THF and precipitated from 750 mL of methanol, filtered and dried in a vacuum oven at 70 °C resulting in a yellow powder (12.9 g, 49%).  $M_{\rm n} = 35\ 300,\ M_{\rm w}/M_{\rm n} = 1.34$ .

## Block copolymer of acetoxystyrene–styrene with monoazofunctionalized unimer (MAz-PAS-PS-T)

**MAz-PAS-PS-T** was synthesized by polymerizing **MAz-PAS-T** with styrene under bulk conditions as illustrated in Scheme 6. A mixture of **MAz-PAS-T** (3.00 g) and styrene (18.2 g, 175 mmol) was heated at 135 °C under nitrogen for 2 h. The polymerization mixture was dissolved in 50 mL of THF and precipitated from 750 mL of methanol, filtered and dried in a vacuum oven at 70 °C resulting in an off-white – yellow powder (5.49 g).  $M_{\rm n} = 40\,400$ ,  $M_{\rm w}/M_{\rm n} = 1.54$ .

# Random copolymer of acetoxystyrene–styrene with monoazofunctionalized unimer (MAz-PAS/PS-T)

MAz-PAS/PS-T was synthesized by polymerizing

acetoxystyrene and styrene with monofunctionalized unimer **8** under bulk conditions as illustrated in Scheme 7. A mixture of **8** (0.1 g, 0.20 mmol), styrene (12.7 g, 123 mmol) and acetoxystyrene (7.45 g, 45.0 mmol) was heated at 135 °C under nitrogen for 2 h. The polymerization mixture was dissolved in 50 mL of THF and precipitated from 750 mL of methanol, filtered and dried in a vacuum oven at 70 °C resulting in a yellow powder (4.36 g).  $M_{\rm n} = 16400$  g/mol,  $M_{\rm w}/M_{\rm n} = 1.24$ .

#### Synthesis of monofunctionalized azobenzene poly(4hydroxystyrene) (MAz-PHS-T) (19)

**MAz-PHS-T** was synthesized by hydrolysis of **MAz-PAS-T** as illustrated in Scheme 8. Concd. ammonium hydroxide (1.5 mL) in 5 mL of water was added dropwise to a 0.5 g solution of **MAz-PAS-T** in 20 mL of methanol. The reaction mixture was refluxed at 65 °C under nitrogen and was stopped after 24 h and was left to cool at room temperature. The polymer was precipitated from 200 mL of water, filtered and dried in an oven at 50 °C to yield yellow crystals (0.20 g, 40%).

# Polymerization of acetoxystyrene with triazofunctionalized unimer (TAz-PAS-3T)

**TAz-PAS-3T** was synthesized by polymerizing acetoxystyrene with **10** under bulk conditions as illustrated in Scheme 9. A mixture of trifunctionalized unimer **10** (0.10 g, 0.07 mmol) and acetoxystyrene (26.6 g, 164 mmol) was heated at 135 °C under nitrogen for 75 min. The polymerization mixture was dissolved in 50 mL of THF and precipitated from 750 mL of methanol, filtered and dried in a vacuum oven at 70 °C resulting in a yellow powder (13.66 g, 51%).  $M_{\rm n} = 74400$ ,  $M_{\rm w}/M_{\rm n} = 1.49$ .

# Block copolymer of acetoxystyrene–styrene with triazofunctionalized unimer (TAz-PAS-PS-3T)

**TAz-PAS-PS-3T** was synthesized by polymerizing **TAz-PAS-3T** with styrene under bulk conditions as illustrated in **Scheme 10**. A mixture of **TAz-PAS-3T** (3.00 g) and styrene (18.2 g, 175 mmol) was heated at 135 °C under nitrogen for 45 min. The polymerization mixture was dissolved in 50 mL of THF and precipitated from 750 mL of methanol, filtered and dried in a vacuum oven at 70 °C resulting in an off-white – yellow powder (6.13 g).  $M_n = 126\ 000$ ,  $M_w/M_n = 1.64$ .

### Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support.

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