Synthesis and characterization of low-molecular-weight azo-acetoxystyrene and azo-naphthalene oligomers via stable free radical polymerization (SFRP)

Dildar Ali, Zaheer Ahmed, Peter M. Kazmaier, and Erwin Buncel

Abstract: As an approach toward controlled molecular architecture through stable free radical polymerization (SFRP), we have prepared a series of oligomers of controlled molecular weights (M_n) and low polydispersities (structures **2** and **3**, with *n* values ranging from 2 to 52). Definitive evidence of structure was obtained through MALDI/MS (inter-peak interval of 162 *m*/*z* in azo-acetoxystyrene oligomers **2** and 260 *m*/*z* in azo-naphthalene oligomers **3**, which correspond to the acetoxystyrene (AS) and naphthalenic (Np) repeating units, with corroborative evidence from NMR and GPC. Two synthetic pathways were explored. Pathway 1 yields azo-acetoxystyrene oligomer **2** via SFR addition of a TEMPO-capped unimer **1** to acetoxystyrene. Subsequent reactions would convert **2** into **3**. In an alternative pathway 2, SFR addition of **1** to 4-(1-methoxynaphthyl)styrene gives azo-naphthalene oligomer **3** directly. Thus, the present reported methodology for controlled architecture has achieved synthesis of oligomers from low M_n (chlorobenzene, PhCl, solvent) to relatively high M_n (bulk), with incorporation of naphthyl (donor) and azobenzene (acceptor) moieties, as well as spacer moieties, in a controlled manner.

Key words: azo-acetoxystyrene oligomers, azo-naphthalene oligomers, stable (controlled) free radical polymerization.

Résumé : Comme approche à une architecture moléculaire contrôlée par le biais d'une polymérisation à l'aide de radicaux libres stables (PRLS), on a préparé une série d'oligomères de masses moléculaires (M_n) contrôlées et de faibles polydispersités (structures **2** et **3**, avec des valeurs de *n* allant de 2 à 52). Les données définitives permettant de déterminer les structures ont été obtenues par spectrométrie de masse avec ionisation laser assistée par une matrice de désorption (SM-ILAMD) [intervalle entre pics de 162 *m*/*z* dans les oligomères azo-acétoxystyrène **2** et de 260 *m*/*z* dans les oligomères azo-naphtalène **3** qui correspondent aux motifs constitutifs de l'acétoxystyrène (AS) et naphtalénique (Np)] et corroborées par RMN et par chromatographie par perméation de gel (CPG). On a exploré deux voies de synthèse. La voie 1 conduit à l'oligomère azo-acétoxystyrène **2** par le biais d'une addition à l'aide de radicaux libres stables (RLS) de l'unimère **1** couvert d'un groupe tétraméthylpipéridine oxyle (TEMPO) à l'acétoxystyrène. Des réactions subséquentes devraient permettre de transformer le produit **2** en **3**. Dans une voie alternative 2, une addition à l'aide de radicaux libres stables aux 4-(1-méthoxynaphtyl)styrène conduit directement à l'oligomère azo-naphtalène **3**. La méthodologie rapportée ici pour obtenir une architecture contrôlée a permis de réaliser la synthèse d'oligomères à partir de produits de masses moléculaires basses (chlorobenzène, PhCl, solvant) à des masses moléculaires relativement élevées (en bloc), avec l'incorporation de portions naphtyles (donneur) et azobenzène (accepteur) ainsi que de portions agissant comme d'espacement d'une façon contrôlée.

Mots-clés : oligomères de l'azo-acétoxystyrène, oligomères de l'azo-naphtalène, stable (contrôlée), polymérisation par radicaux libres.

Introduction

As part of a research program in materials science, we have been engaged in studies of light harvesting (LH) systems and underlying energy transfer (ET) processes.[1–4] Energy transfer and (or) electron transfer are basic to the process of light harvesting and processes such as photosynthesis.[5–10] In turn, the efficiency of ET has been shown to require specific architecture that, typically, incorporates energy donor (**D**) and energy acceptor (**A**) moieties, as shown in Scheme 1. The donor group(s) absorb light energy, which is then transferred from the excited **D** group (**D***), with varying degrees of efficiency, to the acceptors. In principle, electron transfer could also occur, depending upon **D** and **A** groups incorporated in the LH system.

Considerable effort has gone into understanding the pho-

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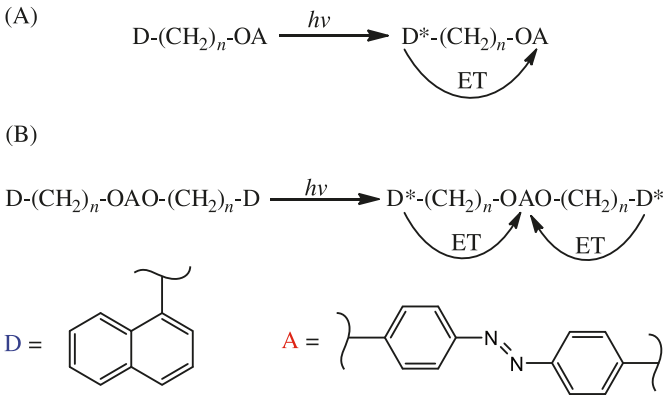
Scheme 1.



tochemical and photophysical processes involved in light harvesting and this effort is, partly, reflected in the range of authoritative reviews that have appeared lately.[11–16]

We have taken a two-pronged approach to probing LH systems. First and in common with a number of research groups,[5,6,17,18] we have prepared a range of dendrimer and starburst polymeric LH model systems, including azobenzene moieties as **A** groups and naphthalenes as **D** moieties.[1–4] Second, we have prepared two LH model systems (Scheme 1) using naphthalene **D** and azobenzene **A** groups tethered by methoxy linkages: **A**–(OCH_2)–**D** and **D**–(CH_2O)–**A**–(OCH_2)–**D**. Our study of the photophysical/chemical properties of two models (Scheme 1) revealed a new criterion for efficiency of energy transfer, involving ratios of rate constants for cis–trans isomerization and ratios of light energy absorption; the LH models were each compared to relevant benchmark molecules. According to this new criterion, energy transfer was virtually complete for both model systems. Electron transfer, under the conditions studied, was not found to be feasible. However, a need for a greater loading of light harvesting donor groups was also identified, as a pre-requisite to the preparation of more practical LH systems.[4] To this end, we have now prepared a series of oligomers **3** containing an azobenzene acceptor group at one end of the chain and a progressively larger number of donor naphthalenic repeating units, as shown in Scheme 2. The long-term goal is to study the LH **3** to **4** interconversion and the photophysics involved (Scheme 2).

Herein, we describe our synthetic strategy, which is based on stable free radical polymerization (SFRP, also termed nitroxide-mediated polymerization, NMP)[19–27] to yield LH oligomers in a controlled manner. SFRP has proven to be particularly valuable in the preparation of polymers with controlled architecture. The Georges,[21,23] Hawker,[20,22,25] Fischer,[19] and Matyjaszewski[26] groups, among others, have pioneered and elaborated on this approach to the preparation of high-molecular-weight polymers. Our aim here, however, is the preparation of low-molecular-weight oligomers for the purpose of preparation of controlled oligomeric structures. The starting point in two different synthetic approaches is the same: the azobenzene-containing unimer, **1**, which is capped reversibly with the persistent nitroxyl radical TEMPO. Reaction of the **1** with 4-acetoxystyrene, **5**, was expected to give low-molecular-weight oligomers **2** (Scheme 2, pathway 1) incorporating the acetoxystyrene repeating unit, *n,* for subsequent conversion of acetoxy functions to naphthyl methoxy donor groups, i.e., formation of **3**. In an alternative preparation (Scheme 2, pathway 2), the SFRP process involved addition oligomerization of 4(1-methoxynaphthyl)-styrene, **6**, with the unimer **1** to give **3**. The results of preparation of the LH models containing 4-(1-methoxynaphthyl)styrene donor repeating units and their characterization (MALDI-TOF/MS and GPC analyses), as well as corroborative NMR analyses, will be discussed in terms of optimization of reaction time and the use of a suitable solvent to control the molecular weight.

Results and discussion

Synthetic strategy

Two synthetic approaches (Scheme 2, pathways 1 and 2), which differed in the structure of the arylvinyl monomer oligomerized with unimer **1**, were examined as routes to the target oligomers, **3**. Addition under SFRP conditions of the benzylic radical derived from **1** (arising from facile scission of the C–O bond of the TEMPO cap) to 4-acetoxystyrene, **5**, should yield oligomers, **2**, with a range of acetoxystyrene repeating units, *n*. Hydrolysis of **2** followed by functionalization with a naphthyl moiety yields the azonaphthyl oligomer **3**.

The alternative route (Scheme 2, pathway 2) consists of SFRP-style addition of the benzylic radical of **1** (formed as before) to the 4-(1-methoxynaphtyl)styrene, **6**, should again give models, **3**.

The difference in the two routes lies, then, in whether the naphthyl donor group is incorporated into the product **3** after oligomerization (pathway 1) or, alternatively, preparation of a suitable arylvinyl monomer, **6**, leads to direct oligomerization to give **3** (pathway 2).

In the preparation of model **3**, controlled low-molecular-weight oligomers were desired. To this end, both the reaction medium and the reaction times were empirically optimized. For the azo-acetoxystyrene oligomerization to yield **2**, bulk (at 130 °C) and solution media (at 120 °C) were studied, where varying amounts, i.e., 1:1 to 1:5 *w/w* ratios of the arylvinyl monomer to chlorobenzene (PhCl) solvent,[20,22,25,28] were used. Reaction times were varied from 1 min to 5 h in a given set of solvent conditions by quenching a reaction run by pouring the reaction mixture into excess cold methanol (~10 mL). For the azo-naphthalene oligomerizations to yield **3** directly, only the solution conditions (i.e., dilution with PhCl at 120 °C) were studied, as a consequence of the information gleaned from the results in the azo-acetoxystyrene systems, **2**. Reaction times were varied from 10 min to 1 h, again as prompted by the results in the related oligomerization system.

The results of these two preparatory routes are listed in Tables 1 and 2 and will be discussed below.

Azo-acetoxystyrene oligomers, 2

The results of the SFRP between the unimer **1** and 4-acetoxystyrene, **5**, as the arylvinyl monomer, are summarized in Table 1. Specifically, the reaction conditions including reaction times, the analysis of the maximum number of acetoxystyrene repeating units (*n*) as determined by MALDI-TOF/MS,[29–31] the number average molecular weight of the

Scheme 2.

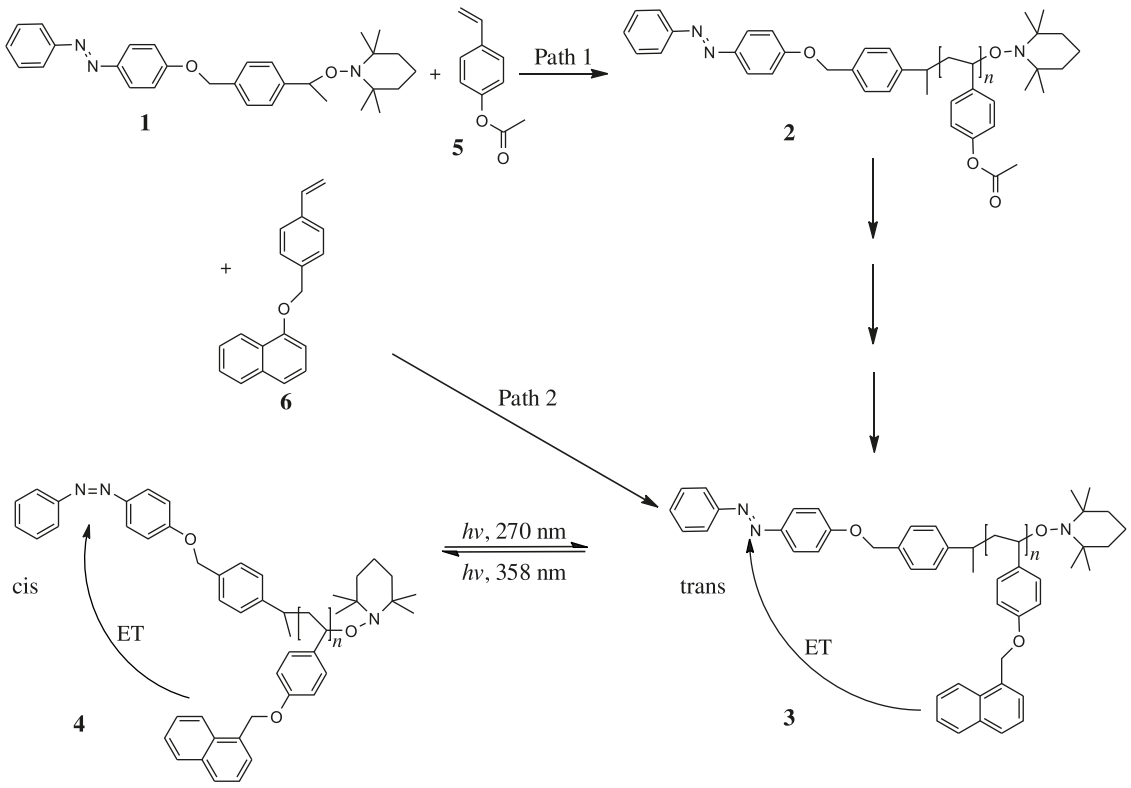


Table 1. Characterization of azo-acetoxystyrene (AS) oligomers, **2**, as a function of reaction conditions: MALDI-TOF/MS and GPC results.

Conditions (*w*/*w* ratio AS:PhCl)	Reaction time (min)[a]	MALDI/MS repeating units n[b]	GPC (M_n,[c] kDa (PD))[d]
A = Bulk			
A-1, A-2, A-3, A-4	1, 3, 5, 10	0,[e] 37, 50, 52	0,[e] 6.7(1.6), 7.8(1.4),8.2(1.3)
B = 1:1			
B-1, B-2, B-3	5, 30, 240	25, 30, 39	4.6(1.4), 5.3(1.3), 9.7(1.3)
C = 1:2			
C-1, C-2, C-3	5, 20, 90	0,[e] 5, 10	NA[f]
D = 1:3			
D-1, D-2, D-3	5, 20, 114	0,[e] 20, 24	0,[e] 5.1(1.2), 8.49(1.1)
E = 1:4			
E-1, E-2, E-3	5, 20, 90	0,[e] 7, 17	NA
F = 1:9			
F-1, F-2, F-3	5, 20, 300	0,[e] 0,[e] 0[e]	0,[e] 0,[e] 0[e]

[a]Bulk reactions were carried out at 130 °C. Solution reactions with PhCl diluent were carried out at 120 °C. Both were quenched by addition to cold MeOH accompanied by precipitation of oligomeric product(s) at times cited.

[b]n is the maximum number of repeating acetoxystyrene (AS) units in **2** observed (±5%–10% error).

[c]Number average molecular weight (kDa) from GPC, calibrated with polystyrene standards.

[d]Polydispersity, M_w/M_n.

[e]Peaks (m/z) corresponding to oligomer formation were not observed; the only major peak recorded is ascribed to the parent molecular ion for protonated azobenzene unimer at $[M + H]^{\bullet+}$ = 472. Oligomer formation was not observed in GPC traces.

[f]NA: not applicable.

oligomers (M_n) as determined by GPC, as well as the polydispersity (PD = M_w/M_n) are listed in the Table.

Mechanistic effects on oligomerization

As can readily be seen in Table 1, even at short reaction times, bulk conditions (experiment series A) yield relatively long chain oligomers, **2**. For example, a 3 min reaction time produces **2** with M_n of 6.7 kDa, corresponding to about a maximum of 37 acetoxystyrene repeating units (n = 37), and a relatively broad molecular weight distribution (PD = M_w/M_n = 1.4). In fact, repetition of the oligomerization at a somewhat lower temperature (120 °C here versus 130 °C in

Table 2. Characterization of azo-naphthalene oligomers, **3**, as a function of reaction conditions: MALDI-TOF/MS and GPC results.

Conditions (*w*/*w* ratio AS:PhCl)	Reaction time (min)[a]	MALDI/MS repeating units n[b]	GPC (M_n,[c] kDa (PD))[d]
Q = 1:3			
Q-1, Q-2	15, 40	2, 12	0.75 (1.2), 3.8 (1.3)
R = 1:4			
	10	2	0.69 (1.1)
S = 1:5			
	30	10	2.5 (1.2)
T = 1:49			
	60	5	1.8 (1.1)

[a]Solution reactions (PhCl diluent) were carried out at 120 °C and were quenched by addition to cold MeOH accompanied by precipitation of oligomeric product(s) at times cited.

[b]n is the maximum number of repeating 4-(1-methoxynaphthyl)styrene (Np) units in **3** observed (±5%–10% error).

[c]Number average molecular weight (kDa) from GPC, calibrated with polystyrene standards.

[d]Polydispersity, M_w/M_n.

the bulk system) and with an equal weight of chlorobenzene (experiment series B) requires 240 min (B-3) to yield **2** with approximately the same number of repeating units (according to MALDI/MS), i.e., n = 39. Representative MALDI/MS spectra for experimental series C-1 to C-3 are shown in Fig. 1 and illustrate the number of repeating units, n, analyzed via this method.

These results are consistent with the mechanism of SFRP, where at the temperature of the reaction the TEMPO-capped unimer **1** dissociates to give persistent TEMPO nitroxyl radical and a resonance-stabilized benzylic radical.[32] The benzylic radical concentration is partitioned between recombination with the TEMPO radical and addition to 4-acetoxystyrene, **5**. Under bulk conditions, the TEMPO-benzylic radical pair is effectively caged by **5**, the arylvinyl monomer. Addition of the benzylic radical to the vinyl functional group of the surrounding acetoxystyrenes should be facile, and relatively high M_n oligomer, **2**, arises in accord with the results listed in Table 1. Recombination of TEMPO with the growing benzylic radical end of the chain provides a termination step in the chain mechanism, and through potential further dissociation, provides an avenue for conversion to a "living" chain mechanism.

Chlorobenzene solvent effects on oligomerization

In principle, addition of chlorobenzene solvent could have two effects.[20,22,25,28] The first and presumably smaller effect is a solvent effect on the dissociation of the unimer. Preferential solvation of the dissociated radicals (e.g., via π–π stacking) relative to the bulky TEMPO-capped unimer could favour dissociation of the unimer. On the other hand, the concentration of acetoxystyrene in the cage surrounding the radical pair would be reduced as a function of increasing added PhCl and the probability of addition to the vinyl group reduced. At short reaction times, the number of repeating groups incorporated in the oligomer would be reduced, as is observed (Table 1).

Generally, then, increasing dilution (Table 1, experiment series C through F) leads to lower-molecular-weight oligomer at comparable reaction times. At 5 min, a 1:1 dilution (AS:PhCl, B-1) gives an oligomer, **2**, incorporating 25 repeating units according to MALDI/MS analysis, while with all other series, a 5 min reaction time yields no oligomer detectable by MALDI/MS or GPC. The results at 20 min appear anomalous; a 1:2 dilution (AS:PhCl; Table 1, C-2) yields an oligomer with five repeating units, while 1:3 dilution (D-2) gives 20 repeating unit oligomer and 1:4 dilution gives seven repeating-unit oligomer, but 1:9 dilution (F-2) yields no detectable oligomer, **2**.

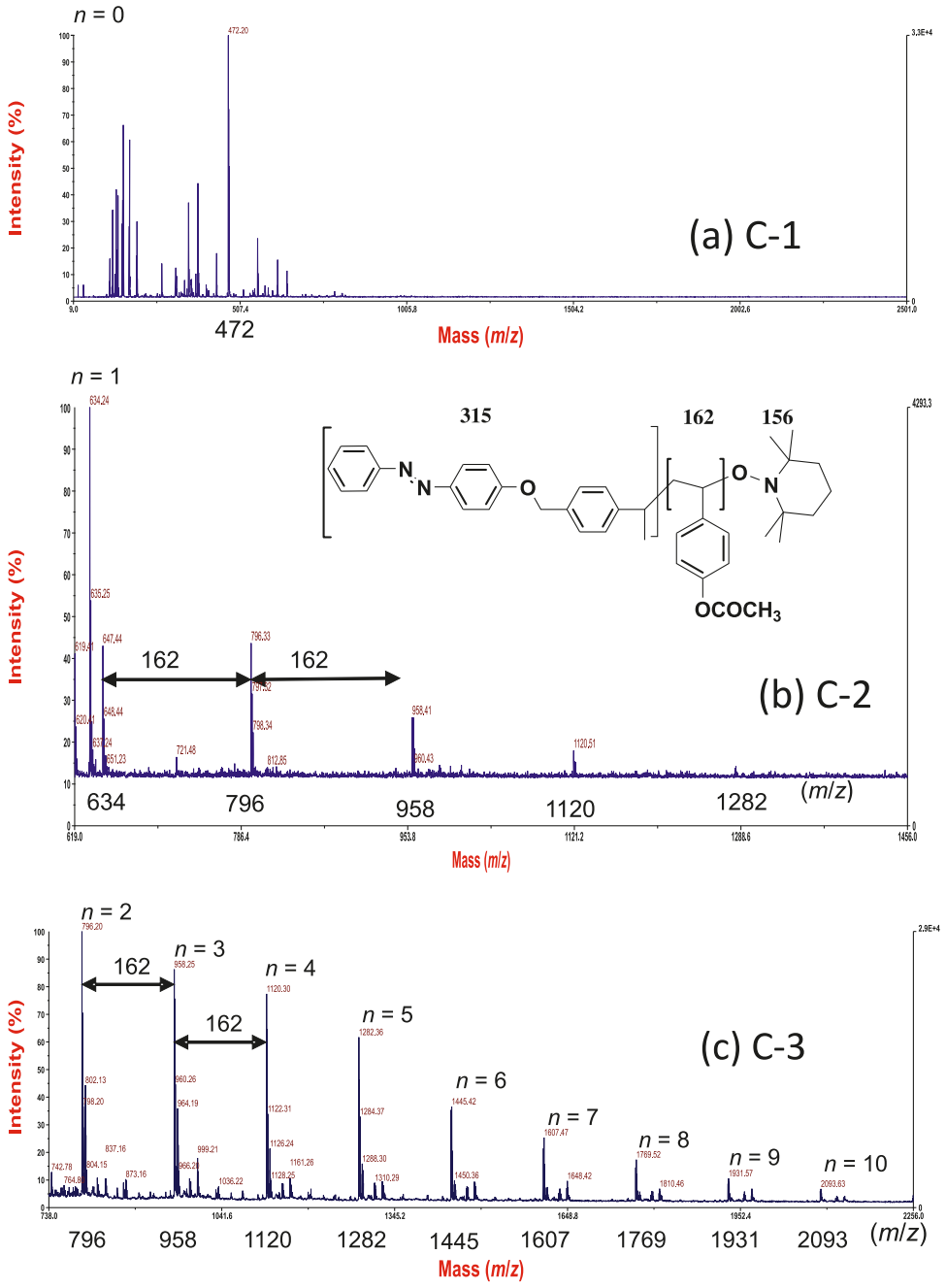
One possibility that accounts for the observed behaviour, namely, an increase in number of repeating units for D-2, as compared to the C-2 and E-2 experiments (Table 1), is that the solvent effect of dilution (i.e., preferential stabilization of the dissociated radicals that would favour dissociation) opposes the concentration effect, that would reduce the probability of radical addition to the arylvinyl monomer. In short, dilution favours dissociation freeing the benzylic radical derived from **1** to add to the vinyl function of **5**, but the decreased concentration of the styrene counteracts this effect partly. The interplay of these factors could lead to the behaviour observed.

At extreme dilution (series F), none of the reaction times studied (5 to 300 min) were sufficient to lead to any oligomer formation. The radicals derived from **1** are effectively free in solution but the concentration of AS is too low to lead to oligomerization.

Also in accord with the foregoing interpretation are the polydispersities determined by GPC (Table 1). In Fig. 2, the GPC traces for experimental series B, D, and F (Table 1) are shown. The bulk run even at 3 min reaction time (Table 1, A-1) gives a PD of 1.6, and modest dilution (B-1, 5 min) yields only a somewhat narrower molecular-weight distribution (PD = 1.4). In living polymerizations, an effective equilibrium is established between dormant or dead polymer (oligomer). This arises from recombination of the benzylic radical end of the growing chain and the TEMPO radical, on the one hand, and propagation of the chain by addition of the benzylic radical to the arylvinyl monomer, on the other. The closer the PD value is to 1 (i.e., monodispersity), the more nearly the polymerization is considered a living process. With a 1:3 dilution with PhCl (D-2, 20 min), the PD drops to 1.3.

The relatively low overall mass recovery found for the acetoxystyrene oligomer **2** indicated that additional steps

Fig. 1. MALDI/MS spectra of azo-acetoxystyrene oligomers with varying acetoxystyene repeating unit (n) values: (a), n = 0; (b), n = 5; (c), n = 10, corresponding to experiments C-1, C-2, and C-3, respectively (see Table 1).



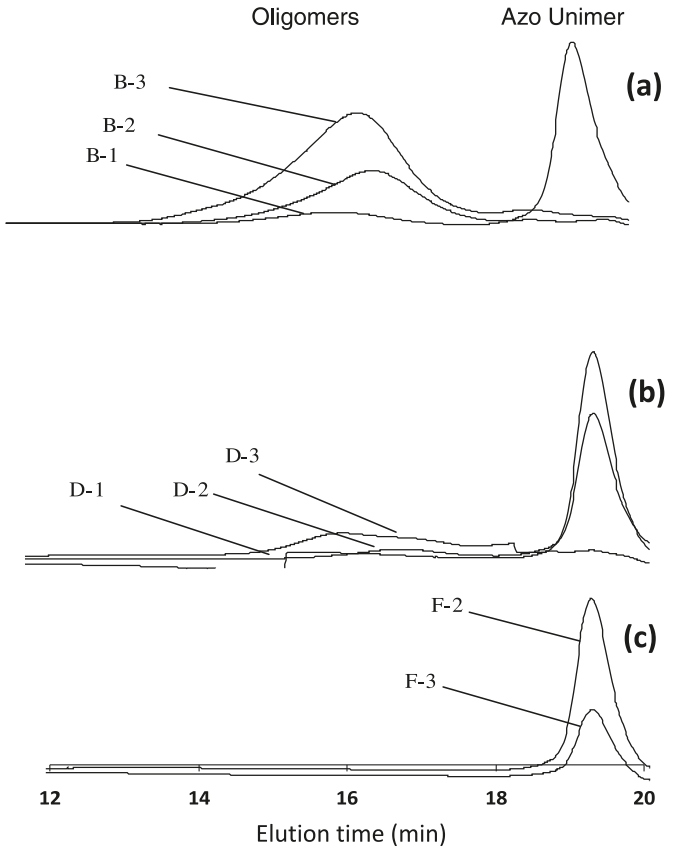
leading to the desired LH-model oligomer, **3**, could result in little final product. The time-consuming nature of the necessary oligomer characterization at each subsequent step was another consideration that prompted us to consider direct incorporation of the naphthalenic donors (Np) in the SFRP step (Scheme 2). However, the results of the preparation of oligomer **2** indicated that dilutions of 1:3 to 1:5 could yield the appropriate LH oligomer **3** comprising a controlled range of repeating donor units.

Azo-naphthalene oligomers, 3

SFRP using unimer **1** and 4-(1-methoxynaphthyl)styrene, **6**, under the range of conditions identified as favouring formation of low-molecular-weight oligomer **2**, was undertaken to prepare **3** directly (Scheme 2). Table 2 summarizes the MALDI-TOF/MS and GPC characterization of **3**.

With a ratio of 1:3 of the arylvinyl monomer, **6**, to PhCl solvent (120 °C; experiment Q, comparable to the D series of experiments in Table 1), SFRP yields low average molecular weight oligomer (M_n = 0.75 kDa) with low polydispersity (PD = 1.2). MALDI/MS analysis shows the expected inter-peak m/z interval of 260 that corresponds to the naphthalenic repeating unit (Np) as shown in Fig. 3 for experiment R. At 15 min reaction time (experiment Q-1), the

Fig. 2. GPC chromatograms for experiments (a) B (B-1, B-2, B-3); (b) D (D-1, D-2, D-3); and (c) F (F-2, F-3) (see Table 1).



maximum number of repeating units found was two; the "oligomer" here consists solely of unimer and dimer. An increase in reaction time to 40 min (Q-2) gives higher-molecular-weight oligomer (M_n = 3.9 kDa; 12 repeating units by MALDI/MS analysis) with only a slight broadening of the molecular weight distribution (PD = 1.3 by GPC). Note, for comparison, that at 20 min reaction time in the acetoxystyrene series (Table 1, D-2), MALDI/MS analysis gave oligomer **2** containing a maximum of 20 repeating units and GPC traces indicated a number average molecular weight of 5.1 kDa for the oligomer with a PD of 1.2, all similar to the results obtained here for experiment Q-2 with a reaction time of 40 min. Clearly, the experimental conditions optimized for the acetoxystyrene SFR oligomerizations (Scheme 2, pathway 1) extend reasonably to the 4-(1-methoxynaphthyl)styrene additions, i.e., formation of **3** directly via pathway 2 in Scheme 2.

Reasonably, the considerations of solvent enhancement of the dissociation of the unimer **1** and the opposing influence of dilution on the addition step apply consistently to pathway 2 to give **3**. It follows that experiments R (1:4, **6**:PhCl solvent) through T (1: 49, **6**:PhCl; Table 2) mimic the trend in degree of oligomerization and polydispersity found for the comparable experimental series D through F (Table 1) found for pathway 1. The number average molecular weight of the oligomer increases, according to GPC, in going from R (1:3) to T (1:4), i.e., from 0.69 kDa to 2.5 kDa with similar PD values and in a maximum number of repeating units of two rising to 10 in the latter run. Experiment T gives an oligomer with a lower maximum number of repeating units (n = 5) and a lower number average molecular weight (1.8 kDa). This parallelism, namely, first increase and then decrease in molecular weight and maximum number of repeating units, which was found in the acetoxystyrene oligomerization runs to give **2**, is consistent with the behaviour found in the oligomerization to give **3**. The same reasons appear to apply: compensatory interplay of solvent and dilution effects on the SFRP chain mechanism.

Highlights of characterization and fractionation

MALDI-TOF/MS

Figure 1 shows the MALDI-TOF/MS analysis[29–31] for three experimental runs (Figs. 1a to 1c, C-1 to C-3, Scheme 2, pathway 1). As can be seen in run C-1, no acetoxystyrene oligomer **2** formed (i.e., n = 0); the major MS peak corresponds to unmodified unimer **1** ($M - H^+$ = 472 m/z) while in the subsequent runs, C-2 and C-3, the major peaks correspond to the oligomers with n = 5 and n = 10, repeating units, respectively. Significantly, for C-2 and C-3, the main fragmentation route involves sequential scission of the acetoxystyrene repeating units. Accordingly, in Fig. 1b, main peaks are seen at n = 5 (m/z = 1282) and at consecutively smaller m/z values with intervals of 162 m/z for n = 4, 3, 2, and 1. This pattern applies equally to C-3 and all experimental runs summarized in Table 1.

An additional feature of these MALDI/MS spectra is the presence of minor peaks at m/z values significantly greater than that of the main peak. Representative is C-2 (Fig. 1b). Arising from the presence of TEMPO radical in the system and multiple benzylic sites for H-abstraction and coupling, the possibility exists for incorporation of *multiple* TEMPO moieties at the oligomeric end groups. This accounts for these higher m/z peaks.

Beyond the major sequential splitting off of repeating units, small fragmentation peaks are evident between the 162 m/z intervals, e.g., between n = 5 and n = 4 in C-3 (Fig. 1c). These small peaks may result from minor defects in the oligomer structure.

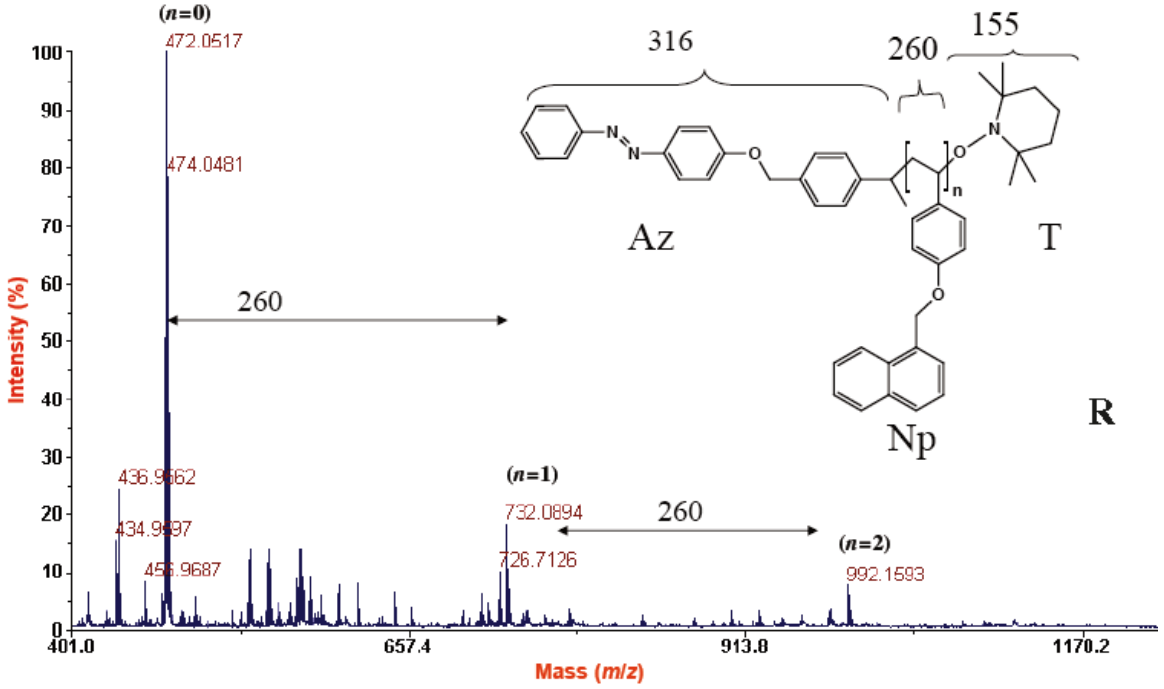
Turning to pathway 2 (Scheme 2), the direct preparation of oligomer **3**, representative MALDI/MS spectra are shown in Fig. 3 for experiment R; reaction conditions are given in Table 2. Once again major peaks result from the oligomer molecular ions with the main fragmentation route involving sequential repeating-unit scission with intervals now of 260 m/z. Minor fragmentation routes for **3** are accounted for as previously outlined for **2** (Scheme 2).

Importantly, the dominant features of the MALDI/MS analysis of **2**, which apply equally to **3**, are the observation of the $M - H^+$ molecular ions corresponding to the maximum number of repeating units in the respective oligomers. Further, the sequential loss of the repeating moiety emphasizes the source of these oligomers: a living SFRP process. Thus, the nature of any minor peaks, arising from impurities or defects, was not investigated in detail, but their presence cannot affect the conclusions or impact the main theme of this study.

GPC

Oligomers **2** and **3** were analyzed by GPC[30] (UV–vis de-

Fig. 3. MALDI/MS spectra for azo-naphthalene oligomer, **3**, experiment R (n = 2).



tector; see Experimental). The results of molecular weight determination (polystyrene calibration) and polydispersity (PD) are summarized in Tables 1 and 2 and discussed earlier in the text (see Fig. 2). Typical GPC traces for 4-(1-methoxynaphthyl)styrene monomer **6** (Fig. 4, experiments R, T, and S) show the separation of oligomeric fractions **3** with elution time, as well as the presence/absence of residual monomer.

^{1}H NMR

^{1}H NMR spectra (Supplementary data, Figs. S2 and S3) for the acetoxystyrene oligomerizations (Scheme 2, pathway 1) are in accord with the MALDI/MS and GPC analyses summarized in Table 1. Specifically, the spectra for oligomer **2** contain a diagnostic signal at 2.27 ppm for the acetoxy methyl of the repeating unit. This signal increases in relative intensity with increasing n values for **2**. Similarly, for samples A-2 to A-4, B-1 to B-3, C-2, and C-3 (Fig. S3), increasingly broad signals are found centred at 6.2 and 6.9 ppm and are ascribed to the aromatic protons of the acetoxystyrene residues. These NMR peaks for the acetoxystyrene repeating unit of **2** are absent in those runs (e.g., A-1) where oligomerization was deemed to be absent, on the basis of MALDI/MS and GPC determinations.

Considering formation of **3** (Scheme 2, pathway 2), ^{1}H NMR spectroscopic analysis agrees with the results given in Table 2 in that higher degrees of oligomerization are accompanied with more intense signals attributable to the Np repeating units and overall broadening of all signals in the relevant spectrum. This is shown in Fig. 5 for experiments T and S.

Fractionation of azo-naphthalene oligomers 3 via flash chromatography

Reaction of a scaled up quantity of **1** and 1-[(4-vinylphenoxy)methyl]naphthalene (20 min; 1:4, monomer:PhCl) yielded a mixture of oligomers containing an oligomer **3** with a maximum of 14 Np repeating units. Flash column chromatography (dichloromethane eluant) gave, after recombination based on TLC, five fractions. The first (H-1) consisted only of unmodified arylvinyl monomer, **6**.

The remaining fractions contained mixtures of oligomers **3**; the longest chain oligomers eluted first. Hence, fraction H-2 contained oligomers with a maximum of 14 Np repeating units according to MALDI/MS. The next in order had n = 8 (H-3), n = 2 (H-4), and n = 1 (H-5).

GPC analysis of the crude reaction product (H) prior to fractionation gave a number average molecular weight of 0.73 kDa with a relatively broad molecular weight distribution (PD = 1.5). Fractions H-2 and H-3 gave GPC peaks corresponding to lower-molecular-weight oligomer (M_n = 0.57 kDa) and narrower distribution (PD = 1.4), while fraction H-4 was found to have M_n = 1.1 kDa with a PD of 1.2. Figure 6 shows an ESI-MS spectrum for oligomer **3** where n = 1 (fraction H-5).

The results show that the number of Np repeating units, n, in the oligomer **3** (via pathway 2 in Scheme 2) and the corresponding molecular weight with low polydispersity (Table 2) may be achieved through careful control of the SFRP reaction conditions (temperature and dilution with PhCl). The oligomeric mixture may be further fractionated by standard flash chromatography.

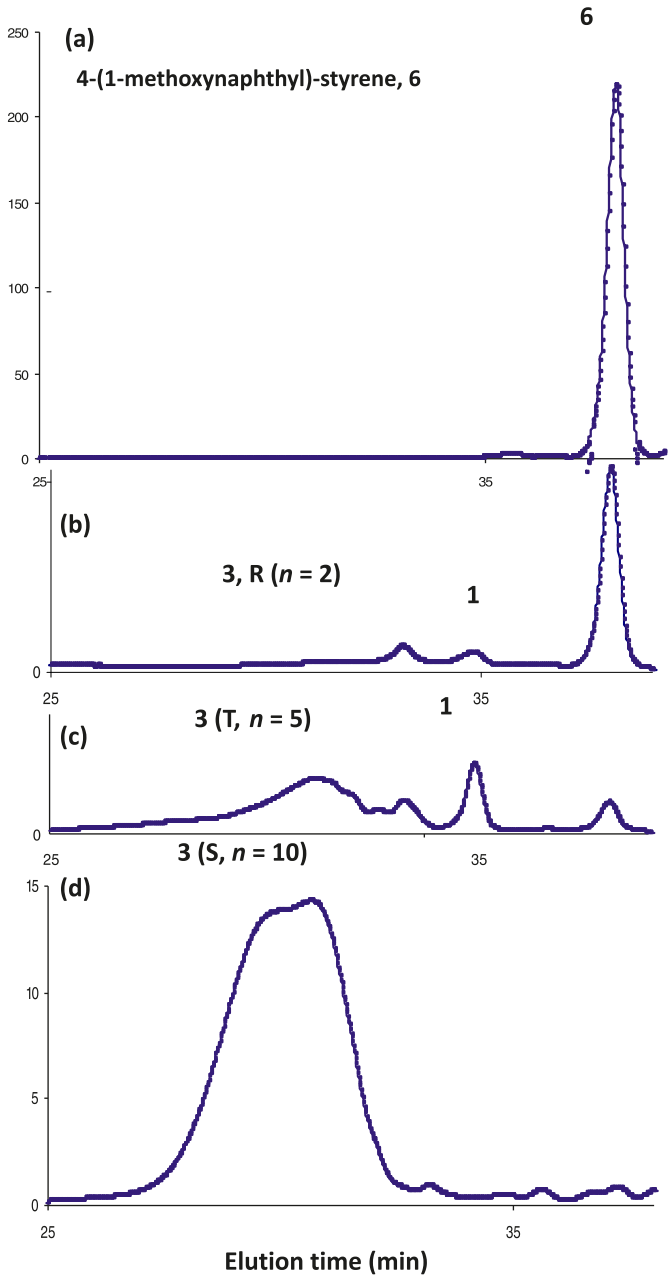
In conclusion, it can be envisaged that the described methodology will lead to a controlled range of oligomers, varying in the numbers of naphthalenic donor units.

Experimental

Instruments and materials

^{1}H NMR spectra were recorded using a Bruker Avance-

Fig. 4. GPC chromatograms showing the increasing molecular weights of **3** and peaks for **1**, **3**, and **6** (Scheme 2), experiments R, T, and S.



400 spectrometer operating at 400.1 MHz, broad band probe, auto-tuned. All chemical shifts are reported as δ in parts per million (ppm) relative to residual $CHCl_3$ (δ = 7.28 ppm) and $CHDCl_2$ (δ = 5.30 ppm) in $CDCl_3$ (source: CDN) and CD_2Cl_2 (CDN) solvents, respectively. Coupling constants (*J*) are reported in Hz. IR samples were recorded using a Bomem MB-120 FTIR spectrophotometer. Dilute samples dissolved in a suitable volatile solvent were allowed to evaporate to provide a film on a KBr plate. Melting points were measured using a Fisher–Johns melting point apparatus and are reported as uncorrected. Gel permeation chromatography (GPC) was performed using Waters 2695 HPLC (Waters 410 differential refractometer detector, 40 °C) with a separation module consisting of four Waters Ultrastyragel® (HR5.0, HR3.0, HR1.0, and HR0.5) in series. Distilled THF was used as eluant with a flow rate of 1.0 mL min^{-1}. The GPC system was calibrated with standard polystyrenes up to an elution time of 35 min. MALDI-TOF/MS traces were recorded using an Applied Biosystems Voyager DE-STR MALDI-time of flight/mass spectrometer with a nitrogen laser (337 nm), delayed extraction and reflectors. An accelerating potential of 20 kV was used in the MS detector in both linear and reflector modes. The optimum matrix used for oligomer characterization was 2,5-dihydroxybenzoic acid (DHB) containing no added salt. Typically, oligomeric samples were prepared by mixing a THF solution of the oligomer(s) (1 mg mL^{-1}) with a solution of DHB (20 mg mL^{-1} in 1:1 MeCN:MeOH) in 1:1 (*v*/*v*) proportions to give the analytical matrix. A 1 μL aliquot of the analytical matrix was placed onto a sample plate and the solvent was evaporated at room temperature to give the MALDI-TOF/MS sample for characterization.

All common solvents (acetone, THF, and so forth) used in the preparations outlined below were purchased commercially in HPLC-grade or better and, where necessary, were further purified by standard methods.[33] 4-Hydroxyazobenzene (Aldrich) was recrystallized from ethanol and THF (VWR) was dried over and distilled from sodium metal/benzophenone. All inorganics (e.g., $NaBH_4$) and the remaining requisite chemicals and organic reagents were purchased commercially and used without further purification. 4-Acetoxystyrene (96%, Aldrich), di-*t*-butyl peroxide (3.5 mol/L in decane, Aldrich), 18-crown-6 (98%, Aldrich), 4-ethylbenzaldehyde (98%, Aldrich), oxalyl chloride (95%, Aldrich), and 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO, gift of Xerox Research Canada) were used as received.

The azo unimer **1** was prepared in a five-step procedure as previously described[1,27] starting from 4-ethylbenzaldehyde that was reduced with $NaBH_4$ to 4-ethylbenzyl alcohol, converted to the bromide, and capped with 2,2,6,6-tetramethyl-1-piperidinoxyl) using TEMPO and di-*t*-butylperoxyoxalate. Further reaction with NaI in acetone converted the bromide to the iodide, which, in a final step, was reacted with 4-hydroxyazobenzene in the presence of K_2CO_3 and 18-crown-6 in acetone to give **1**. The overall yield of this five-step procedure was 24%. All physical and spectroscopic properties were in good agreement with those previously published.[1] The MALDI/MS of **1** contained small extraneous peaks at greater *m*/*z* values than the protonated molecular ion for **1** (i.e., M – $H^{\bullet+}$ at 472.28 *m*/*z*). The minor impurity was not removed by column chromatography (60 mesh silica gel; dichloromethane eluent), and **1** was used as is in the following syntheses.

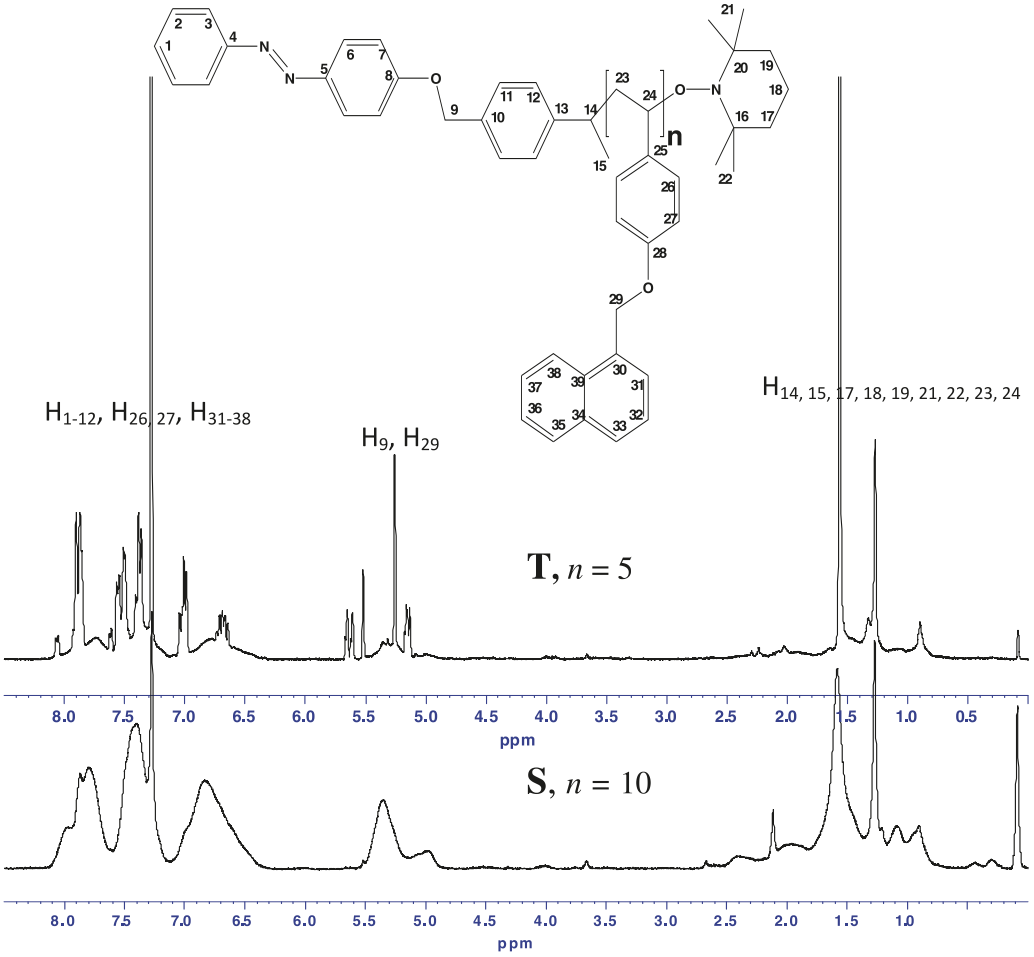
Preparation of azo-acetoxystyrene oligomers, 2

Azo-acetoxystyrene oligomers, **2**, capped with TEMPO were prepared under SFRP reaction conditions via addition of **1** to acetoxystyrene, AS, under bulk and chlorobenzene (PhCl) solvent conditions.

General bulk procedure

Mixtures of **1** and AS were introduced into silicone-septum-capped ampoules (10 mL), swept with N_2, and these were immersed in an oil bath thermostatted to 130 °C. After the

Fig. 5. ^{1}H NMR spectra for azo-naphthalene oligomers, **3**, experiment T (n = 5) and experiment S (n = 10).



set reaction times, each mixture was poured into excess cold MeOH (10 mL) to quench the reaction and the precipitate, in each case, was collected by filtration. The precipitates were dried in vacuo (<1 torr, 50 °C) (1 torr = 133.322 Pa) overnight to give yellow coloured powders.

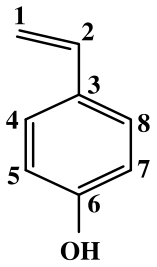
General solvent procedure

Experimental series B–F (cf. Table 1) were carried out at 120 °C. Mixtures of the reagents and PhCl solvent were prepared in ampoules, as given above, and the temperature maintained by immersion of the vials in the thermostatted oil bath. The mass ratios of AS to PhCl are listed in Table 1. Three aliquots were withdrawn via gas-tight syringe from each experimental series at different time intervals to yield a range of oligomeric mixtures, **2**, that were analyzed by MALDI-TOF/MS, ^{1}H NMR spectrometry, IR spectrophotometry, and GPC (UV–vis detector), as outlined in the previous text and in the Results and discussion section.

Table 3 shows molar ratios and amount of PhCl solvent used in each experimental run.

Preparation of azo-naphthalene oligomers, 3

Saponification of 4-acetoxystyrene (10 g, 0.061 mol in 2.5 g MeOH) with KOH (0.25 g, 0.0045 mol), under N_2 atmosphere, followed by acidification (glacial AcOH) and addition of toluene to precipitate any poly(4-hydroxystyrene) gave a colourless solution, after filtration. This filtrate was cooled (~ –70 °C) from which 4-vinylphenol (4-hydroxystyrene) crystallized as colourless crystals (4.5 g, 45%); mp 59–60 °C (lit. 68–69 °C,[34] 73.5 °C[35]). IR (KBr, cm^{-1}) ν: 3249, 2977, 1656, 1541, 1410, 1110, 992, 834, 647. ^{1}H NMR ($[CD_3]_2CO$, 400 MHz) δ: 8.45 (1H, s, O**H**), 7.34 (2H, d, J = 6.8, H-4,8), 6.98 (2H, d, J = 6.8, H-5,7), 6.67 (1H, d,d, 17.6, 10.4, H-2), 5.60 (1H, d, J_{trans} = 17.6, H-1), 5.01 (1H, d, J_{cis} = 10.4, H-1). ^{13}C NMR (CD_3OD, 100 MHz) δ: 157.0, C-6; 136.4, C-5,7; 129.4, C-3; 127.0, C-4,8; 114.9, C-1; 109.4, C-2. EI-MS $(M + H)^+$ m/z: 120.0532 (calcd. for C_8H_8O: 120.0531 g/mol).



4-(1-methoxynaphthyl)styrene

Weighed quantities of 4-vinylphenol (1.04 g, 8.6 mmol), 1-chloromethylnaphthalene (1.2 g, 6.8 mmol), K_2CO_3 (2.05 g, 14.7 mmol), and 18-crown-6 polyether (0.29 g,

Fig. 6. ESI-MS spectrum for oligomer **3** with repeating unit "*n*" equal to 1 after separation with column chromatography (fraction H-5).

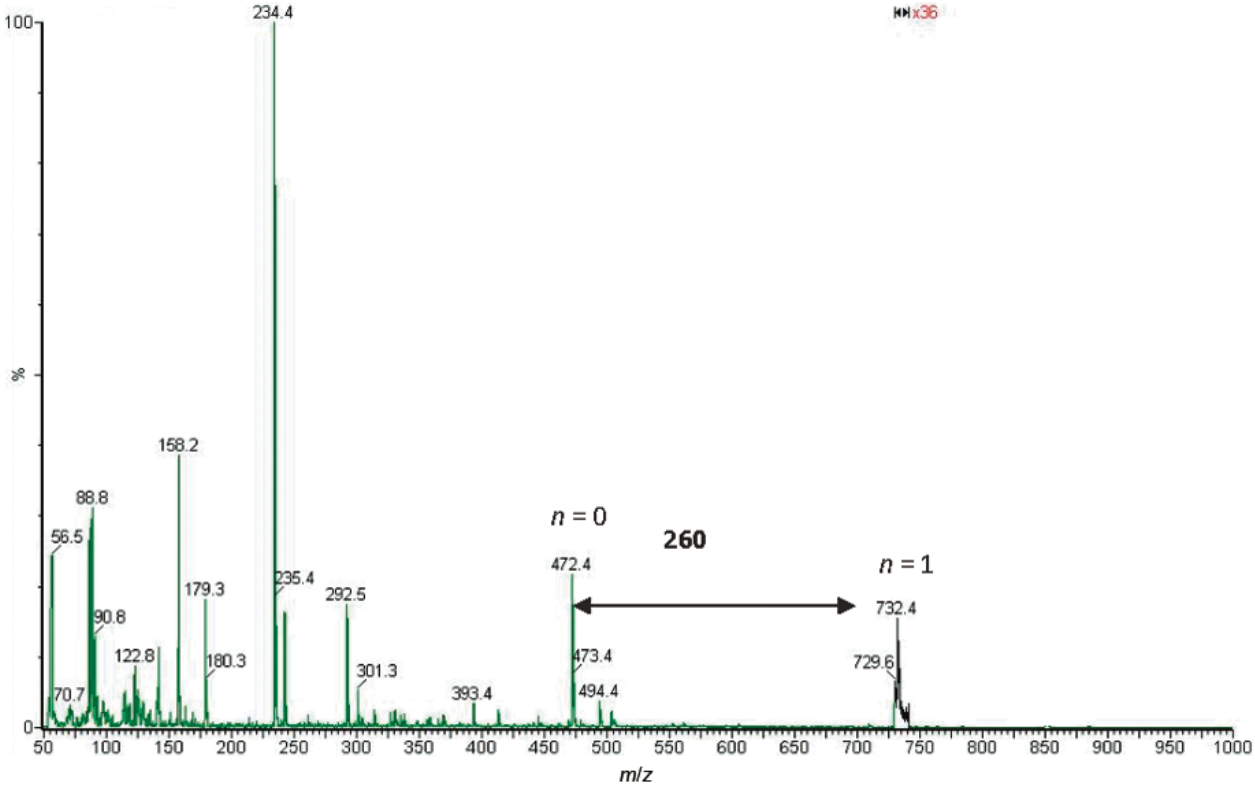


Table 3. Reaction conditions for azo-acetoxystyrene oligomers **2**.

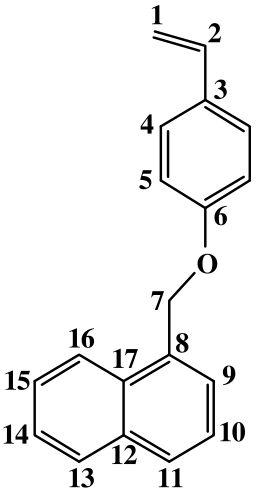
Experimental series	Azo unimer, 1 mg (mmol)	Acetoxystyrene, 5 mg (mmol)	Chlorobenzene (PhCl) mg (mmol)
A-1[a]	10 (0.02)	251 (1.54)	Bulk (monomer solvent)
A-2	10 (0.02)	230 (1.41)	Bulk (monomer solvent)
A-3	10 (0.02)	267 (1.65)	Bulk (monomer solvent)
A-4	10 (0.02)	250 (1.54)	Bulk (monomer solvent)
B	28 (0.06)	170 (1.05)	170 (1.51)
C	31 (0.06)	162 (1.05)	324 (2.90)
D	30 (0.06)	162 (1.05)	487 (4.34)
E	31 (0.06)	162 (1.05)	648 (5.78)
F	31 (0.06)	162 (1.05)	1600 (14.2)

[a]Experiments A-1 through A-4 were performed at 130 °C. All other runs were performed at 120 °C.

Table 4. Azo-naphthalene oligomers **3**. Reaction conditions: 120 °C.

Experiment	1 mg (mol)	6 mg (mmol)	PhCl mg (mmol)	Ratio 6:PhCl (*w*/*w*)	Time (min)
Q-1	12 (0.027)	500 (1.92)	1500 (13.3)	1:3	15
Q-2	12 (0.027)	500 (1.92)	1500 (13.3)	1:3	40
R	13 (0.025)	50 (0.20)	288 (2.57)	1:4	10
S	13 (0.028)	110 (0.42)	600 (5.30)	1:5	30
T	11 (0.024)	50 (0.20)	1 mL	1:49	60

1.1 mmol) were mixed with acetone (25 mL) in a round-bottom flask and the reaction mixture was brought to reflux for 36 h. The acetone was removed under reduced pressure (rotary evaporator) and the residue added to water and dichloromethane. Separation, drying, and evaporation of the organic layer yielded crude product as an oil. This product was purified by column chromatography (CH_2Cl_2/hexane, 1:1 *v*/*v*) to yield after evaporation of solvent colourless crystals of 4-(1-methoxynaphtyl)styrene (1.7 g, 75%); mp 48–50 °C. ^{1}H NMR (CD_2Cl_2, 400 Mz) δ: 8.23 (1H, d, J = 7.6, H-16), 7.99 (1H, d, J = 8.8, H-13), 7.95 (1H, d, J = 8.0, H-11), 7.66 (1H, m, H-15), 7.61 (2H, m overlapping signals, H-10.14), 7.56 (1H, d, J = 8.4, H-9), 7.45 (2H, d, J = 8.0, H-4,4′).



Oligomerization to give 3

Mixtures of **1**, **6**, and PhCl were placed in a 25 mL round-bottomed flask sealed with Teflon rubber septum and purged with N_2 for 5 min prior to immersion in an oil bath stabilized at 120 °C. After selected reaction times (Table 4), the reaction was quenched by addition of copious cold MeOH to give a gummy material that was dissolved upon addition of THF (2 mL). Precipitation of **3** with MeOH and evaporation of solvent in vacuo yielded **3** after filtration; the product was dried under high vacuum (<1 torr) overnight.

Table 4 lists reaction conditions including mole ratios of reagents and reaction times for the preparation of **3**.

Supplementary data

Supplementary data (MALDI-MS traces, ^{1}H NMR spectra, GPC profiles for oligomers) for this article are available on the journal Web site (canjchem.nrc.ca).

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