The Cation Radical Chain Cycloaddition Polymerization of *N*,3-Bis(*trans*-1-propenyl)carbazole: The Critical Importance of Intramolecular Hole Transfer in Cation Radical Cycloaddition Polymerization

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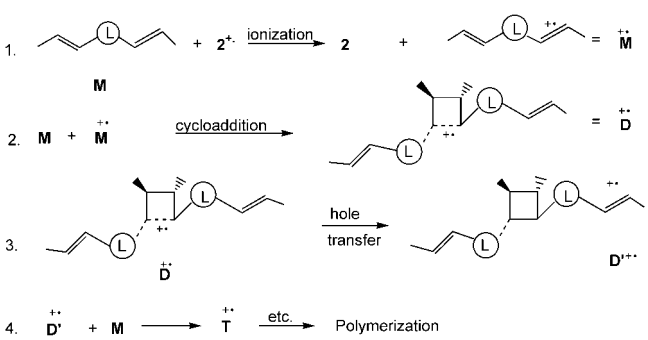
Abstract: The synthesis and polymerization of *N*,3-[bis(*trans*-1-propenyl)]carbazole (**1**) is reported. Using either the stable cation radical salt tris(4-bromophenyl)aminium hexachloroantimonate ($2^{+\cdot}$) or anodic oxidation to initiate the reaction, novel cycloaddition polymers are obtained in which the intermonomer linkages are of the cyclobutane, and to some extent of the Diels–Alder, type. A novel cation radical chain mechanism is proposed for the reaction, and extensive support for this mechanism is presented. The greatly enhanced reactivity of difunctional, as opposed to monofunctional, substrates in cation radical cycloadditions is dramatically highlighted by a comparison of the cycloaddition reactivity (rapid polymerization) of **1** versus *N*-propenylcarbazole (inefficient cyclodimerization) under electrochemical oxidation conditions. The sharply enhanced reactivity of **1** is attributed to the availability of intramolecular hole transfer in the bifunctional but not the monofunctional case.

Keywords: carbazole; cation radical; cycloaddition; polymerization

Introduction

Cation radical chain cycloaddition represents a fundamentally new and powerful polymerization mechanism which is especially effective for readily ionizable (electron rich and/or conjugated) monomers.[1,2] It is unique among polymerization methods in that it works best for propenyl rather than vinyl monomers and provides intermonomer linkages which are of the cycloaddition (cyclobutane or Diels–Alder) type under very mild conditions. It is not related to polymerization mechanisms which, although initiated by cation radical formation, are propagated cationically *via* coupling of two initially formed cation radicals to give dications.[3] Further, although certain polymerizations, such as those of thiophene and pyrrole, are considered to proceed *via* cation radical intermediates, these reactions appear to require the stoichiometric generation of cation radicals, i.e., they are by no means either chain or catalytic processes.[4] Of course, neither cationic polymerizations initiated by cation radical formation nor stoichiometric cation radical polymerizations result in cycloaddition polymerization. Finally, since cycloaddition requires two unsaturated functionalities as reactants, cycloaddition polymerization requires bifunctional monomers, unlike linear polymerization methods. These latter, including such traditional methods as radical, cationic, and anionic polymerization, often afford insoluble, network polymers when applied to bifunctional monomers. Although it is of relatively recent vintage, several instances of efficient cation radical chain polymerizations have now been reported.[1,5] Like other (monofunctional) cation radical cycloaddition chemistry, these polymerizations



M = monomer; D = dimer; T = trimer; L = linker

Scheme 1.

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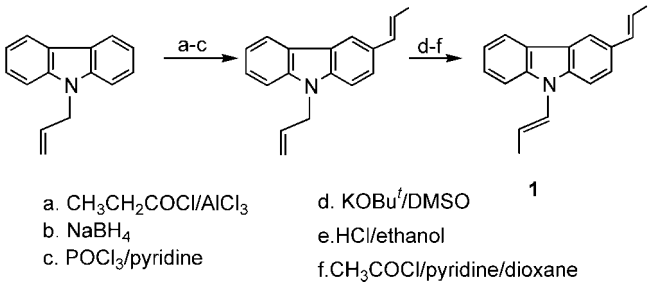
are extremely efficient even when carried out at 0 °C and are often complete within 1 – 2 minutes or even less. The mechanism proposed for a generalized cation radical chain cyclobutanation reaction is illustrated in Scheme 1.

Results and Discussion

Polyvinylcarbazole (PVK) and related carbazole-containing polymers are very frequently the polymers of choice for hole transport (HT) in emerging applications such as photorefractive (PR) polymers and organic light-emitting diodes (OLED's).[6] This research group has recently reported the efficient cation radical chain cycloaddition polymerization of 3,6-bis-(*trans*-1-propenyl)carbazole to afford a novel polymer structure which contains the carbazole units in the main polymer chain, in contrast to the pendant carbazole units of PVK. The observed cycloadditions were found to be of a novel Diels–Alder type in which a π-bond of the carbazole ring participates as part of the dienic component. The present paper describes the synthesis and polymerization of a new monomer, *N*,3-bis(*trans*-1-propenyl)carbazole (**1**), to afford still another type of carbazole polymer in which the predominant intermonomer linkage is of the cyclobutane type. It is noteworthy that both main chain carbazole polymers[7] and carbazole polymers having cyclobutane linkages in the main chain[8] have been identified as of special interest in respect to their PR properties. The synthesis of **1** is illustrated in Scheme 1. A novel and potentially useful aspect of this synthesis is the use of the *N*-allyl group as both a protecting group for ring acylation of carbazole and as a propenyl group equivalent, the latter through the subsequent base-catalyzed isomerization of the *N*-allyl group. However, this isomerization yields a mixture of *cis*- and *trans*-*N*-propenyl groups, which is quite difficult to separate chromatographically. The pure *N*-*trans*-propenyl monomer (**1**) was obtained very efficiently from the mixture by first converting it to the 1-ethoxypropyl derivative (HCl/ethanol), followed by elimination of ethanol from the latter (acetyl chloride/pyridine/dioxane). This elimination results in the exclusive formation of the *trans*-*N*-propenyl derivative (**1**). The use of the *N*-allyl group as a convenient protecting group for the nitrogen atom of carbazole appears attractive in a more general sense, since the propenyl group can undoubtedly be hydrolytically removed in dilute aqueous acid in a manner analogous to the reaction with ethanol.

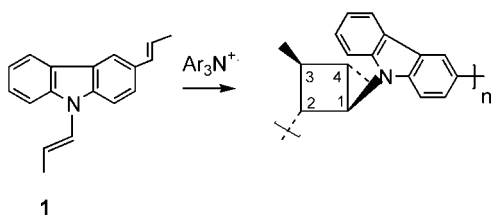
The polymerization of **1** (Scheme 3) was initiated by two distinctly different methods. The chemical method consists of treating a solution of **1** in dichloromethane at 0 °C with a dichloromethane solution containing 15 mol % of tris(4-bromophenyl)aminium



Scheme 2.

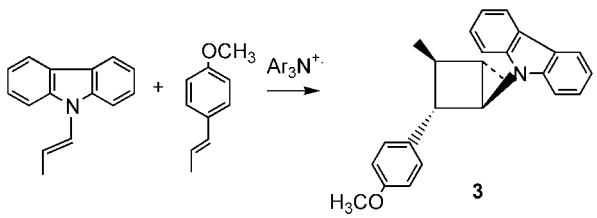
hexachloroantimonate ($2^{+\cdot}$).[9] The reaction, under these conditions, is complete within 1 min and affords a soluble polymer having M_W = 8780 (PDI 7.3). The electrochemical method consists of subjecting a dichloromethane/acetonitrile solution of **1**, which also contains lithium perchlorate as the electrolyte and 2,6-di-*tert*-butylpyridine as a hindered base to inhibit any potential acid-catalyzed chemistry, to anodic oxidation at a vitreous carbon anode, using a potential of +0.65 V vs. SCE. The monomer was completely consumed within 1 h, after 14.9 coulombs of current had passed, and work-up yielded a polymer (M_W = 6240; PDI = 4.49) the NMR of which is virtually superimposable upon that obtained from the aminium salt-initiated polymerization. Both polymers show broad absorptions in the ^{1}H NMR at the following chemical shifts, δ = 0.6 – 1.3 (CH_3), 1.7 – 2.0 (CH_3), 2.0 – 2.3 (propenyl end groups), 2.6 – 2.8 (C3 proton), 3.3 – 3.5 (C4 proton), 4.2 – 4.4 (C2 proton), 4.4 – 4.7 (C1 proton), in addition to the absorptions of the aromatic protons.

Although these spectra appeared to be generally consistent with expectation for the unsymmetrical cyclobutapolymer of Scheme 3, it appeared desirable to synthesize a non-polymeric model compound of known and closely related structure for a closer comparison. Interestingly, but unfortunately, we were unable to obtain any of the desired cross adduct in an attempted reaction between two monofunctional molecules which closely model the functionality present in **1**, namely *N*-propenylcarbazole and *N*-phenyl-3-propenylcarbazole, under aminium salt conditions. This result alludes to the crucial importance of having both the *N*-propenyl and the 3-propenyl groups in the same molecule, i.e., to the importance that intramolecularity plays in the reactions of **1**. As an approximate model compound, the cross adduct be-



Scheme 3.

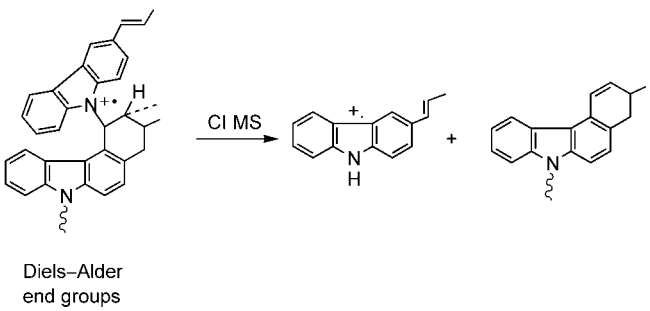
tween *N*-propenylcarbazole and *trans*-anethole was successfully prepared (Scheme 4). The ^{1}H NMR spectrum of this cross adduct is indeed quite closely comparable in the aliphatic region to that of the polymer, δ = 1.06 and 1.48 (the two non-equivalent methyl groups), 1.82 – 1.96 (C3 proton), 2.96 – 3.05 (C4 proton), 3.71 (the methoxy methyl protons), 4.01 (the C2 proton), 4.55 (the C1 proton). The existence of major amounts of cyclobutane linkages formed by the symmetrical coupling of two *N*-propenyl groups is ruled out, since the cyclobutane dimers of *N*-propenylcarbazole (**3**) have equivalent C1 and C2 protons which absorb at much lower fields (δ 5.8). Although the symmetrical cyclobutane dimer of *N*-phenyl-3-propenylcarbazole (**4**) does have benzylic protons which absorb at δ = 4.2, there are, of course, no other aliphatic proton absorptions below this (specifically no absorption at δ = 4.6). Further, the absence of symmetrical cyclodimerization of two *N*-propenyl groups suggests that there is little likelihood of symmetrical cyclodimerization of two C3-propenyl groups, which would have to accompany the dimerization of *N*-propenyl groups. On the other hand, the unsymmetrical cyclodimerization of an *N*-propenyl group with a C3-propenyl group provides both of the δ = 4.2 and 4.6 absorptions, as well as the two non-equivalent methine protons as C3 and C4 of the cyclobutane linkage.



Scheme 4.

Mass spectrometric data provide further strong support for the existence of predominant intermonomer linkages of the cyclobutane type. The CI MS of the polymer prepared under electrochemical oxidation conditions has its parent ion at a mass/charge ratio which corresponds to that of the monomer cation radical (**1**$^{+\cdot}$). The fragmentation of the molecular cations of cyclobutane adducts is well known to be extremely facile[10] and the parent ion in such a spectrum is normally the molecular ion corresponding to an alkene fragment formed by retrocyclobutanation involving the weakest cyclobutane bond. Such cleavage is not observed for acyclic addition products formed *via* carbocation mechanisms. Further, although Diels–Alder adducts may undergo the retro cation radical Diels–Alder reaction, typically these do not produce diene or dienophile fragments as the parent ion. Importantly, in the present case, retrocycloaddition of Diels–Alder adduct linkages is not expected at all, because previous work establishes that the initial Diels–Alder adducts formed by conjugate addition to an aromatic ring rapidly re-aromatize to structures which are even less capable of retro Diels–Alder reactions.[5]

Significantly, the CI MS of this same polymer also has a substantial peak corresponding to the molecular weight of 3-(*trans*-1-propenyl)carbazole (Scheme 5). The formation of this ion, which has no substituent upon the nitrogen atom, is not expected of cyclobutane adduct linkages, but is just what one might expect from the presence of some Diels–Alder linkages. The Diels–Alder type linkages which, by analogy to the previous research, should be formed from **1** are seen to have a terminal 3-propenylcarbazole moiety attached to a benzylic position of another carbazole ring. Generation of a cation radical site upon this terminal carbazole moiety could easily result in the formation of the cation radical of 3-(*trans*-1-propenyl)carbazole by a cyclic β-elimination process. It therefore appears likely that, although cyclobutane linkages are predominant in this polymer, there is a significant fraction of Diels–Alder linkages as well.



Scheme 5.

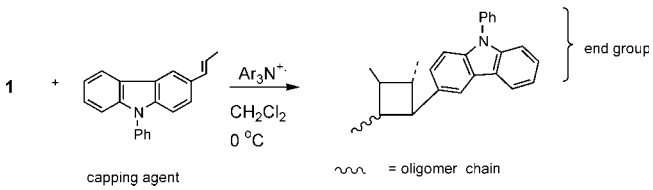
Re-Initiation of Polymerization

Another unique aspect of cation radical chain cycloaddition polymerization is the capability for re-initiating polymerization *via* ionization of the propenyl end groups of the polymer. When the purified polymer obtained from the aminium salt-initiated polymerization of **1** (M_W = 8780) is subjected to an additional treatment with tris(4-bromophenyl)aminium hexachloroantimonate under the same conditions as before, the molecular weight of the isolated polymer is increased to M_W = 17700 (PDI = 4.0).

Capping Experiments

It has been previously established that cation radical chain cycloaddition polymerizations are readily capped at lower degrees of polymerization (DP's) by corresponding monofunctional molecules (capping agents).[5] In the present research, the capping of the

polymerization of **1** by both types of functionality present in **1** (*N*- and 3-propenylcarbazole functionalities) was studied (Scheme 6). When an excess (3:1) of *N*-phenyl-3-propenylcarbazole was employed as a capping agent in conjunction with the polymerization of **1**, a mixture of oligomers was formed. The chromatographically purified mixture of oligomers could not be individually separated into monodisperse compounds, but it was established by means of mass spectrometry, molecular weight distribution, and mass balances that they consisted mainly of "tetramers" (two molecules of **1** and two of the capping agent) and "trimers" (one molecule of **1** and two of the cap) along with smaller amounts of higher oligomers. Thus the M_W was found to be 1330 (PDI = 2.0), compared to 1060 expected for this type of tetramer. Further, the mass of the capping agent incorporated into the mixture of oligomers corresponded to an approximately 1:1 molar ratio of monomer and capping agent. Moreover, the ^{1}H NMR spectrum of this oligomer mixture revealed the absence of olefinic hydrogens, indicating that propenyl end groups were not present and thus that capping groups must be present at essentially all of the oligomer termini. Finally, CI mass spectrometric analysis revealed the predominant presence of the 2 + 2 tetramer with substantial amounts of trimers, and lesser quantities of pentamers and hexamers. Similar results were obtained when capping was carried out with a 1:1 ratio of **1** and the capping agent. That the polymerization was efficiently capped in itself indicates the operation of a cation radical chain process. More specifically, the presence of a capping cyclobutane moiety is indicated by the presence in the CI and FAB MS of a strong peak for the positive fragment corresponding to the cap (*m/e* = 284; M+1). In the EI MS this peak was by far the dominant peak (i.e., the parent ion). As has been previously noted, the cation radicals of cyclobutane adducts are well known to fragment extensively in just this manner. Corresponding capping studies using *N*-propenylcarbazole also generated a mixture of polymers and oligomers, the latter consisting of mostly trimers and tetramers.



Scheme 6.

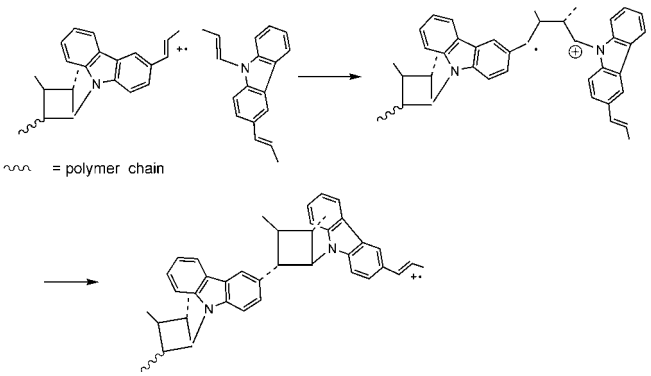
Electrochemical Studies

The polymerization of **1** under anodic oxidation conditions has previously been noted. The formation of a polymer which is essentially identical to that formed in the aminium salt-induced reaction is significant since acid-catalyzed, carbocation-mediated processes are not normally encountered under electrochemical conditions and especially in the presence of added hindered base. For a relevant comparison of the reactivity of monomer **1** with the reactivity of *N*-propenyl groups in a monofunctional substrate, the electrochemical oxidation of *N*-propenylcarbazole was studied under conditions identical to those used for the polymerization of **1** except that an anodic potential was applied (0.45 V vs. SCE) which was approximately equal to the oxidation potential of *N*-propenylcarbazole (E_{ox} = 0.38 V vs. SCE). After a reaction time identical to that used for **1** (1 h; 17.0 coulombs of current), the reaction mixture was worked-up and analyzed by NMR spectroscopy. The recovered material consisted predominantly of unreacted *N*-propenylcarbazole, with only trace amounts of the cyclobutane dimers of this substrate. The observation of the formation of these cyclobutane dimers does confirm the operation of cation radical cyclodimerization to the exclusion of other (e.g., cationically propagated) processes, but the recovery of predominantly *N*-propenylcarbazole emphasizes the inefficiency of the cation radical dimerization of this monofunctional substrate as contrasted to the polymerization of **1**. Thus, both the absence of acid-catalyzed or carbocation-mediated processes and the presence of relatively inefficient cation radical chemistry is confirmed.

These observations concerning the relative reactivity of **1** and *N*-propenylcarbazole are further substantiated by cyclic voltammetry (CV) studies. While the CV scans of both *N*-propenylcarbazole and *N*-phenyl-3-propenylcarbazole (the monofunctional analogues of **1**) appeared to be reversible and temporally stable, that of **1** was not. Significantly, the peak corresponding to the first peak oxidation potential of **1** completely disappeared after the first scan and could not be found at all on subsequent scans. The *N*-propenyl groups of **1** were thus completely reacted within 1 s. The new oxidation potential observed after the first scan (+0.59 V) corresponds approximately to that expected from oligomers having only terminal 3-propenyl groups.

Mechanistic Considerations

The much greater reactivity of the cation radical of **1** than either of the corresponding monofunctional analogues is of fundamental interest. That the enhanced reactivity of **1** is not merely the result of having complementary functional groups present is also indicated by the failure of the attempted reaction of *N*-propenylcarbazole with *N*-phenyl-3-propenylcarbazole. A plausible explanation for this phenomenon is nicely provided by the propagation mechanism

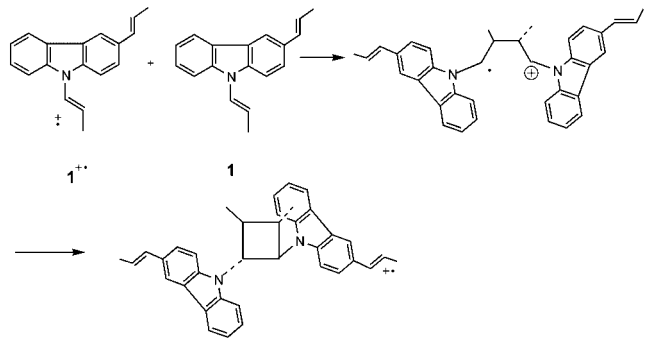


Scheme 7.

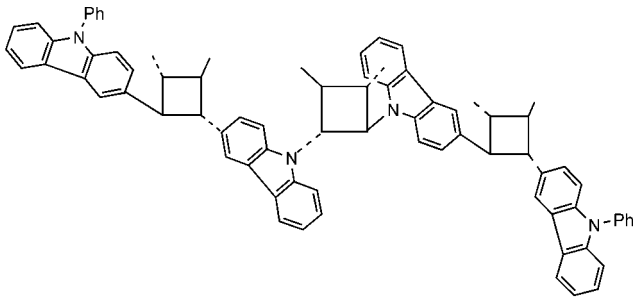
proposed in Scheme 7. In the first step, a cation radical centered upon a 3-propenyl group preferentially reacts with an *N*-propenyl group (as opposed to the 3-propenyl group) of monomer **1** to yield a distonic cation radical with the positive charge centered upon the carbon atom bearing the nitrogen substituent. Since the *N*-propenyl group is essentially an enamine function, it is anticipated that this functionality would be more reactive than a 3-propenyl function toward the electrophilic cation radical functionality. The second, ring closure, step is then facilitated by the presence of the 3-propenyl functionality, since the 3-propenyl substituent provides important additional delocalization and stabilization of the cation radical moiety (hole) compared to that available in the case of an unsubstituted carbazole cation radical, such as that formed in the case of cycloaddition to monofunctional *N*-propenylcarbazole. The result is the regeneration of a 3-propenylcarbazole type cation radical which again preferentially reacts with an *N*-propenyl function of **1** to continue the same propagation cycle.

Initiation

Although the details of the mechanism of initiation of the polymerization of **1** are less certain, the electrochemical studies, along with the capping studies, combine to suggest a probable initiation mechanism (Scheme 8). The oxidation potential measurements reveal that *N*-propenylcarbazole (E_{OX} = 0.36 V) is substantially more easily ionized than *N*-phenyl-3-propenylcarbazole (E_{OX} = 0.60 V). Consequently, although the cation radical moiety of $\mathbf{1}^{+\cdot}$ must be delocalized over both the *N*- and 3-propenyl functions, it appears likely that there is greater hole density (cation radical character) on the *N*-propenyl group and that reactivity at this site is probably preferred. The previously noted preference of cation radicals for reacting at the more nucleophilic double bond of the enamine function would then suggest initial dimerization predominantly between two *N*-propenyl functions, with subsequent ring closure of the distonic cation radical and hole transfer to the 3-propenyl moiety. This proposal is further supported by the observation that, even in the presence of a 3:1 ratio of capping agent (*N*-phenyl-3-propenylcarbazole), the main product of oligomerization is the 2 + 2 "tetramer" (Scheme 9), and not a doubly capped monomer ("trimer").



Scheme 8.



Scheme 9.

Conclusions

The synthesis of *N*,3-[bis(*trans*-1-propenyl)]carbazole (**1**) in eight steps has been accomplished. The polymerization of this new monomer using either the stable cation radical salt tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{2}^{+\cdot}$) or anodic oxidation to initiate the reaction yielded soluble carbazole-containing polymers having weight-average molecular weights ranging from 7000 to 18000 and having intermonomer linkages which are of the cyclobutane, and to some extent of the Diels–Alder, type. A novel cation radical chain cycloaddition mechanism is proposed for the reaction, and extensive support for this mechanism is presented. The greatly enhanced reactivity of difunctional, as opposed to monofunctional, substrates in cation radical cycloadditions is dramatically highlighted by a comparison of the cycloaddition reactivity (rapid polymerization) of **1** versus a closely related monofunctional analogue, *N*-propenylcarbazole (inefficient cyclodimerization) under comparable electrochemical oxidation conditions. The sharply enhanced reactivity of **1** is attributed to the availability of intramolecular hole transfer in the bifunctional but not the monofunctional case.

Experimental Section

General Remarks

Proton and carbon NMR spectra were recorded on a Bruker AC250 or a Varian UNITY PLUS 300 spectrometer. Chemical shifts (δ) are relative to tetramethylsilane, and coupling constants (*J*) are in Hz. High resolution mass spectra (HRMS) were recorded on a VGZAB-2E mass spectrometer. GC measurements were recorded using a Hewlett-Packard 6890 instrument with an HP 6890 Series Integrator. All chemicals used as starting materials were purchased from the Aldrich Company and used as received unless otherwise specified. The dichloromethane solvent was dried by refluxing it over calcium hydride. The catalyst, tris(4-bromophenyl)aminium hexachloroantimonate, was synthesized according to a literature procedure.[9] Gel permeation chromatography (GPC) analysis of molecular weight distributions was performed on all polymer samples using two 10 μm mixed-bed Perkin-Elmer PL gel columns connected to a Waters 410 differential refractometer. The GPC was calibrated with monodisperse polystyrene standards. The mobile phase was anhydrous THF, at a flow rate of 1.0 mL/min. Cyclic voltammetry (CV) measurements were carried out using platinum disks as both the working and counter electrodes. The ferrocene/ferrocinium ion couple was used as an internal reference.

N-Allylcarbazole

To a vigorously stirred mixture of NaOH (35 g, 0.87 mol), 35 mL of water, 5 mL of dry benzene, phase-transfer catalyst benzyltriethylammonium chloride (410 mg, 1.8 mmol) and carbazole (10.63 g, 0.87 mol), allyl bromide (10.9 g, 0.09 mol) was added at a rate which ensured the vigorous boiling of the mixture. Stirring was continued further for 3 h at room temperature, and the mixture was then poured into ice/water and left overnight. The precipitate was filtered and washed with water several times. The filtered product was subjected to recrystallization in ethanol, and *N*-allylcarbazole was obtained; yield: 7.81 g (63%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.92 (dd, *J* = 4.8, 1.8 Hz, 2H), 5.08 (d, *J* = 17.1 Hz, 1H), 5.21 (d, *J* = 10.3 Hz, 1H), 5.97 – 6.09 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H). 8.18 (d, *J* = 7.6 Hz, 2H); LRMS: *m/z* =208; HRMS: calculated for $C_{15}H_{14}N$: 208.112625, found: 208.11914.

N-Allyl-3-propionylcarbazole

To a dry three-necked, round-bottom flask equipped with a magnetic stirrer, 9-allylcarbazole (7.81 g, 0.038 mol) was added, followed by dry benzene (70 mL). After lowering the temperature of the reaction in an ice bath, propionyl chloride (3.84 g, 0.042 mol) was added, followed by the slow addition of $AlCl_3$ (6.54 g, 0.049 mol). After the addition was complete, the reaction mixture was stirred for an additional 1.5 h. The reaction mixture was then carefully poured into a separatory funnel containing crushed ice. Aqueous work-up, followed by chromatography on silica gel (hexane/dichloromethane, 9:1, then 1:1) afforded *N*-allyl-3-propionylcarbazole; yield: 3.31 g (34.4%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.2, 7.5 Hz, 3H), 3.13 (q, *J* = 7.2, 7.5 Hz, 2H), 4.91 (dd, *J* = 4.8, 1.8 Hz, 2H), 5.01 (d, *J* = 17.1 Hz, 1H), 5.17 (d, *J* = 10.5 Hz, 1H), 5.91 – 6.04 (m, 1H), 7.27 – 7.39 (m, 3H), 7.49 (t, *J* = 7.8 Hz, 1H), 8.13 (t, *J* = 8.6 Hz, 2H), 8.77 (s, 1H); LRMS: *m/z* = 264; HRMS: calculated for $C_{18}H_{18}NO$: 264.138839, found: 264.138988.

N-Allyl-3-(1-hydroxypropyl)carbazole

N-Allyl-3-propionylcarbazole (3.31 g, 0.013 mol) was reduced with sodium borohydride (0.57 g, 0.015 mol) in 20 mL of ethanol for 11 h at room temperature. After quenching the reaction mixture with 10% aqueous acetic acid, followed by aqueous work-up, the pure alcohol product was obtained; yield: 3.34 g (100%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.2 Hz, 3H), 1.80 – 2.02 (m, 2H), 2.17 (s, 1H), 4.76 (t, *J* = 6.6 Hz, 1H), 4.87 (dd, *J* = 5.1, 1.5 Hz, 2H), 5.04 (d, *J* = 17.1 Hz, 1H), 5.16 (d, *J* = 10.5 Hz, 1H), 5.93 – 6.05 (m, 1H), 7.25 – 7.50 (m, 5H), 8.01 (s, 1H); LRMS: *m/z* = 265; HRMS: calculated for $C_{18}H_{20}NO$: 266.154489, found: 266.154938.

N-Allyl-3-(*trans*-1-propenyl)carbazole

To *N*-allyl-3-(1-hydroxypropyl)carbazole (3.34 g, 0.013 mol) was added dry pyridine (7 mL), followed by the slow addition of $POCl_3$ (2.32 g, 0.015 mol) in an ice bath. After the reaction mixture was heated to refluxing for 1.5 h, it was cooled to room temperature. Water was then added slowly, with the reaction mixture being cooled in an ice bath. After aqueous work-up and column chromatography on silica gel (hexane, then hexane/dichloromethane, 1:1), the pure *N*-allyl-3-(*trans*-1-propenyl)carbazole was obtained; yield: 2.72 g (87.1%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (dd, *J* = 6.9, 1.8 Hz, 3H), 4.87 (dd, *J* = 4.8, 1.8 Hz, 2H), 5.03 (d, *J* = 17.1 Hz, 1H), 5.16 (d, *J* = 10.5 Hz, 1H), 5.92 – 6.04 (m, 1H), 6.61 (d, *J* = 15.6 Hz, 1H), 7.27 – 7.32 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.50 (m, 2H), 8.06 (s, 1H), 8.10 (d, *J* = 7.2 Hz, 1H); LRMS: *m/z* = 248; HRMS: calculated for $C_{18}H_{18}N$: 248.143925, found: 248.143974.

3-(*trans*-1-Propenyl)-*N*-(*trans*- and *cis*-1-propenyl)carbazole

To 2.7 g (0.011 mol) of allyl-3-(*trans*-1-propenyl)carbazole was added dry DMSO (20 mL), followed by the addition of *t*-BuOK (302 mg, 2.69 mmol). The reaction mixture was allowed to stand at room temperature for 1 h. After complete conversion of the starting material, the solution was poured onto ice, and the resulting oily substance was extracted with dichloromethane. After aqueous work-up of the organic layer, followed by chromatography on silica gel (hexane), the product, 3-(*trans*-1-propenyl)-*N*-(*trans*- and *cis*-1-propenyl)carbazole, was obtained; yield: 1.7 g (63.9%). According to the NMR data, the product consisted of a mixture of the *N*-*trans* and *N*-*cis* isomers in a ratio of 2.5:1; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.64 (dd, *J* = 6.9, 1.8 Hz, 3H; *N*-*cis*-propenyl), 1.94 (dd, *J* = 6.9, 1.8 Hz, 3H; *N*-*trans*-propenyl), 2.00 (dd, *J* = 6.9, 1.8 Hz, 3H; 3-*trans*-propenyl), 5.91 – 6.00 (m, 1H; *N*-*cis*-propenyl), 6.01 – 6.16 (m, 1H; *N*-*trans*-propenyl), 6.21 – 6.33 (m, 1H; 3-*trans*-propenyl), 6.59 (dd, *J* = 15.6, 1.8 Hz, 1H; 3-*trans*-propenyl), 6.71 (dd, *J* = 7.8, 1.8 Hz, 1H; *N*-*cis*-propenyl), 6.92 (dd, *J* = 14.1, 1.5 Hz, 1H; *N*-*trans*-propenyl), 7.19 – 7.28 (m, 2H), 7.41 – 7.51 (m, 3H), 7.55 (d, *J* = 8.2 Hz, 1H), 8.00 (s, 1H), 8.03 – 8.10 (m, 1H).

N-(1-Ethoxypropyl)-3-(*trans*-1-propenyl)carbazole

To the preceding mixture of isomers (1.7 g, 6.88 mmol) were added 30 mL of benzene and 20 mL of absolute ethanol, followed by the addition of HCl (6.25 mL of a 0.001M solution in ethanol) at room temperature. The reaction was carried out at room temperature with stirring for 21 h. After aqueous work-up, followed by chromatography on silica gel (hexane, then hexane/dichloromethane, 3:1), *N*-(1-ethoxypropyl)-3-(*trans*-1-propenyl)carbazole was obtained; yield: 1.3 g (64.5%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.5 Hz, 3H CH_3 in ethoxy), 1.14 (t, *J* = 7.2 Hz, 3H; propenyl CH_3), 1.93 (dd, *J* = 6.6, 1.5 Hz, 3H), 2.24 (q, *J* = 7.5 Hz, 2H, CH_2 in ethoxy), 3.28 – 3.43 (m, 2H, CH_2 in propenyl), 5.69 (t, *J* = 6.9 Hz, 1H; propenyl methine), 6.23 – 6.32 (m, 1H), 7.20 – 7.25 (m, 1H), 7.39 – 7.47 (m, 1H), 7.54 – 7.62 (m, 2H), 8.03 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 1H); LRMS: *m/z* = 294; HRMS: calculated for $C_{20}H_{24}NO$: 294.185790, found: 294.184534.

N,3-Bis(*trans*-1-propenyl)carbazole (1)

A 1.2 g (4.1 mmol) sample of *N*-(1-ethoxypropyl)-3-(*trans*-1-propenyl)carbazole was dissolved in 32 mL of anhydrous dioxane, and anhydrous pyridine (3.9 g, 49 mmol) was added. To this solution at room temperature, while stirring, acetyl chloride (1.29 g, 16.4 mmol) was added dropwise. The reaction was continued with stirring at 95 °C for 5 h. After cooling, followed by aqueous work-up, the reaction mixture was subjected to column chromatography on silica gel (petroleum ether:dichloromethane, 9:1). The pure *N*,3-bis(*trans*-1-propenyl)carbazole was obtained; yield: 850 mg (84%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93 (dd, *J* = 6.9, 1.8 Hz, 3H; 3-propenyl), 2.00 (dd, *J* = 6.9, 1.8 Hz, 3H; *N*-propenyl), 6.04 – 6.15 (m, 1H; *N*-propenyl), 6.21 – 6.33 (m, 1H; 3-propenyl), 6.58 (dd, *J* = 15.6, 1.8 Hz, 1H; 3-propenyl), 6.92 (dd, *J* = 14.1, 1.8 Hz, 1H; *N*-propenyl), 7.26 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.51 (m, 3H), 7.55 (d, *J* = 8.1 Hz, 1H), 8.00 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$): δ = 15.6, 18.5, 110.0 (×2), 117.4, 118.2, 119.9, 120.1, 123.3, 123.4, 123.6, 124.0, 124.1, 1245.9, 130.3, 131.4; LRMS: *m/z* = 248; HRMS: calculated for $C_{18}H_{18}N$: 248.143925, found: 248.142830; E_p (peak oxidation potentials) = 0.59 V, 0.96 V vs. SCE.

Polymerization of *N*,3-Bis(*trans*-1-propenyl)-carbazole Using Tris(4-bromophenyl)aminium Hexachloroantimonate (2)

To a stirred solution of tris(4-bromophenyl)aminium hexachloroantimonate (50 mg, 0.061 mmol) in dry dichloromethane (15 mL) at 0 °C under a nitrogen atmosphere was added a solution of *N*,3-bis(*trans*-1-propenyl)carbazole (100 mg, 0.405 mmol) in dry dichloromethane (5 mL). After 1 min the reaction mixture was quenched with an excess of saturated potassium carbonate in methanol. The crude polymer obtained after aqueous work-up was subjected to short column chromatography on silica gel (hexane, then dichloromethane/methanol, 18:1). The pure polymer was obtained; yield: 58 mg (58%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.6 – 1.3 (br), 1.7 – 2.0 (br), 2.0 – 2.3 (br), 2.6 – 2.8 (br), 3.3 – 3.5 (br), 4.2 – 4.4 (br), 4.4 – 4.7 (br), 6.1 – 7.0 (br), 7.0 – 7.8 (br), 7.8 – 8.3 (br); M_W = 8780, PD = 7.3.

Re-Initiation of the Polymerization of the Preceding Polymer

To a stirred solution of tris(4-bromophenyl)aminium hexachloroantimonate (8.3 mg, 0.01 mmol) in anhydrous dichloromethane (20 mL) at 0 °C under a nitrogen atmosphere was added a solution of the preceding polymer (50 mg, 0.202 mmol) in anhydrous dichloromethane (10 mL). After 1.5 min the reaction mixture was quenched with an excess of saturated K_2CO_5 in methanol. After aqueous work-up, polymer was obtained; yield: 50 mg; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.6 – 1.2 (br), 1.5 – 1.8 (br), 1.8 – 2.0 (br), 2.0 – 2.4 (br), 2.6 – 2.8 (br), 3.3 – 3.5 (br), 4.2 – 4.4 (br), 4.4 – 4.7 (br), 6.1 – 7.0 (br), 7.0 – 7.8 (br), 7.8 – 8.3 (br); M_W = 17700, PD = 4.0.

Controlled Potential Electrochemical Polymerization of *N*,3-Bis(*trans*-1-propenyl)carbazole (1)

The electrochemical polymerization of *N*,3-bis(*trans*-1-propenyl) carbazole (**1**) was carried out using an ESC Potentiostat 415,640 Digital Coulometer and 420X Power Supply. A divided electrochemical cell (25 mL) was used where the counter electrode (vitreous carbon) was separated from the bulk reaction chamber by a glass frit. The working electrode (vitreous carbon) and the reference electrode (Ag/Ag^+) were placed in the bulk reaction chamber. To the electrochemical cell were added 82 mg (0.33 mmol) of *N*,3-bis(*trans*-1-propenyl)carbazole (**1**) and 19 mg (0.1 mmol) of 2,6-di-*tert*-butylpyridine dissolved in 17 mL of the electrolyte solution (0.1 M $LiClO_4$ in a 1:3 mixture of acetonitrile and dichloromethane). The counter electrode was filled with electrolyte solution up to the same level. Electrolysis of the substrate was carried out at 0.65 V with stirring at 0 °C under a nitrogen atmosphere. When 14.9 coulombs of current had been passed, the reaction was stopped by quenching with saturated potassium carbonate in methanol. The product was obtained after aqueous work-up; yield: 81 mg (80.2%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.6 – 1.4 (br), 1.6 – 1.8 (br), 1.9 – 2.0 (br), 2.1 – 2.3 (br), 2.6 – 2.8 (br), 3.2 – 3.5 (br), 4.2 – 4.4 (br), 4.4 – 4.7 (br), 5.8 – 6.0 (br), 6.1 – 6.5 (br), 6.5 – 6.8 (br), 6.8 – 7.8 (br), 7.8 – 8.3 (br); LRMS: *m/z* = 208 [corresponding to fragmentation to 3-(*trans*-1-propenyl)carbazole], 248 (corresponding to the monomer fragment, M), 495 (2M + 1), 742 (3M + 1), 1236 (5M + 1); 1482 (6M); M_W = 6240; PD = 4.49

N-(1-Ethoxypropyl)carbazole

To carbazole (20.9 g, 0.125 mol) were added 75 mL of benzene, 10 mL of absolute ethanol, and 14.5 g (0.25 mol) of propanal, followed by the addition of concentrated HCl (56 mg, 1.5 mmol) at room temperature. The reaction mixture was heated at 70 °C with stirring for 4.5 h. After aqueous work-up, followed by recrystallization from ethanol, *N*-(1-ethoxypropyl)carbazole was isolated; yield: 14 g (46%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.5 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 2.25 (p, *J* = 7.4 Hz, 2H), 3.24 – 3.48 (m, 2H), 5.72 (t, *J* = 6.8 Hz, 1H), 7.20 – 7.26 (m, 2H), 7.42 (m, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 8.08 (d, *J* = 7.7 Hz, 2H); LRMS: *m/z* = 254; HRMS: calculated for $C_{17}H_{20}ON$: 253.146664, found: 253.145796.

N-(*trans*-1-Propenyl)carbazole

A 4.4 g (0.017 mol) sample of *N*-(1-ethoxypropyl)carbazole was dissolved in 25 mL of anhydrous dioxane, followed by the addition of anhydrous pyridine (16.5 g, 0.2 mol). To this solution at room temperature, while stirring, was added in a dropwise manner, acetyl chloride (5.29 g, 0.066 mol). The reaction was continued at 95 °C with stirring for 20 h. After cooling, followed by aqueous work-up, the reaction mixture was subjected to column chromatography on silica gel (petroleum ether) to furnish *N*-(*trans*-1-propenyl)carbazole; yield: 2.16 g (62); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.01 (dd, *J* = 6.8, 1.8 Hz, 3H), 6.06 – 6.17 (m, 1H), 6.94 (dd, *J* = 14.0, 1.6 Hz, 1H), 7.23 – 7.29 (m, 2H), 7.42 – 7.48 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 8.07 (d, *J* = 8.5 Hz, 2H); E_{ox} = 0.36, 0.93 vs. SCE.

Controlled Potential Electrochemical Reaction of *N*-(*trans*-1-Propenyl)carbazole

To the electrochemical cell was added 100 mg (0.48 mmol) of *N*-(*trans*-1-propenyl) carbazole and 28 mg (0.15 mmol) of 2,6-di-*tert*-butylpyridine dissolved in 17 mL of the electrolyte solution (0.1 M $LiClO_4$ in a 1:3 mixture of acetonitrile and dichloromethane). The counter electrode was filled with electrolyte solution up to the same level. Electrolysis of the substrate was carried out at 0.45 V with stirring at 0 °C under a nitrogen atmosphere. When 17.0 coulombs of current had passed, the reaction was stopped by quenching with saturated potassium carbonate in methanol. The product (120 mg, 93.8% yield) obtained after aqueous work-up consisted mostly of unreacted starting material, along with trace amounts of a mixture of cyclobutadimers of the reactant.

Aminium Salt-Catalyzed Cross Cycloaddition Between *N*-(*trans*-1-Propenyl)carbazole and *trans*-Anethole

To a solvent mixture consisting of 40 mL of anhydrous dichloromethane and 10 mL of water was added tris(4-bromophenyl)aminium hexachloroantimonate (122.5 mg, 0.15 mmol) at room temperature. The mixture was stirred for 3 min, cooled to 0 °C under a nitrogen atmosphere followed by addition of a solution containing *N*-(*trans*-1-propenyl)-carbazole (207 mg, 1 mmol) and *trans*-anethole (148 mg, 1 mmol) dissolved in 5 mL of dichloromethane. The reaction mixture was quenched after a reaction time of 30 s with saturated potassium carbonate in methanol followed by the usual two-phase, water/dichloromethane aqueous work-up. After column chromatography on silica gel (petroleum ether, then petroleum ether/dichloromethane, 3:1), the pure product was obtained; yield: 155 mg (43.7%); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06 (d, *J* = 6.8 Hz, 3H), 1.48 (d, *J* = 6.6 Hz, 3H), 1.82 – 1.96 (m, 1H), 2.96 – 3.05 (m, 1H) ,3.71 (s, 3H), 4.01 (t, *J* = 9.5 Hz, 1H), 4.55 (t, *J* = 9.5 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 7.18 – 7.24 (m, 2H), 7.39 – 7.45 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 8.57 (d, *J* = 7.6 Hz, 2H).

Oligomerization of *N*,3-bis(*trans*-1-Propenyl)carbazole Capped by *N*-Phenyl-3-(*trans*-1-propenyl)carbazole: 1:1 Molar Ratio of Capping Agent and Monomer

To a stirred solution of tris(4-bromophenyl)aminium hexachloroantimonate (25 mg, 0.03 mmol) in anhydrous dichloromethane (20 mL) at 0 °C under a nitrogen atmosphere was added a solution of *N*,3-bis(*trans*-1-propenyl)carbazole (50 mg, 0.202 mmol) and *N*-phenyl-3-(*trans*-1-propenyl)carbazole (57 mg, 0.202 mmol)[5] in anhydrous dichloromethane (10 mL). After 1.5 min, the reaction mixture was quenched with an excess of saturated potassium carbonate in methanol. The thin-layer chromatogram revealed that the starting materials had completely reacted. After the usual two-phase, water/dichloromethane, aqueous work-up, the reaction mixture was subjected to column chromatography on silica gel (hexane, hexane/dichloromethane, 2:1, then dichloromethane). Two fractions were separated, one containing lower molecular weight oligomers (yield: 20 mg, 18.7%) and the other somewhat higher molecular weight oligomers (yield: 56 mg, 52.3%). *First fraction*: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.8 – 1.1 (br), 1.2 – 1.4 (br), 1.6 – 1.9 (br), 1.9 – 2.1 (br), 2.2 – 2.5 (br), 2.6 – 2.9 (br), 3.1 – 3.3 (br), 3.6 – 3.7 (br), 4.2 – 4.4 (br), 4.5 – 4.7 (br), 5.9 – 6.0 (br), 6.2 – 6.3 (br), 6.5 – 6.9 (br), 6.9 – 7.7 (br), 7.8 – 8.2 (br); LRMS: *m/z* = 284 (M' + 1 ,where M' is the capping agent; *this is the parent ion*), 495 (2M + 1, where M is the monomer), 531 (M + M' + 1), 814 (M + 2M' + 1), 1062 (2M + 2M' + 2), 1309 (3M + 2M' + 2), 1343 (2M + 3M'), 1591 (3M + 3M' + 1); *Second fraction:* ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.8 – 1.4 (br), 1.6 – 1.8 (br), 1.9 – 2.1 (br), 2.5 – 2.9 (br), 3.1 – 3.2 (br), 3.3 – 3.5 (br), 3.6 – 3.7 (br), 4.2 – 4.4 (br), 4.5 – 4.7 (br), 5.9 – 6.1 (br), 6.1 – 6.3 (br), 6.6 – 7.8 (br), 7.8 – 8.2 (br); LRMS: *m/z* = 208 [3-(*trans*-1-propenyl)carbazole + 1], 284 (M' + 1), 495 (2M + 1), 531 (M + M' + 1), 565, 566 (2M'), 778 (2M + M' + 1), 1060 (2M + 2M'), 1342 (2M + 3M' – 1), 1590, 1592 (3M + 3M' + 2), 1837 (4M + 3M'), 1873 (3M + 4M').

Oligomerization of *N*,3-(*trans*-1-Propenyl)carbazole (1) Capped by *N*-Phenyl-3-(*trans*-1-propenyl)carbazole: 1:3 Ratio of Monomer and Capping Agent

To a stirred solution of tris(4-bromophenyl)aminium hexachloroantimonate (198 mg, 0.242 mmol) in anhydrous dichloromethane (20 mL) at 0 °C under a nitrogen atmosphere was added a solution of *N*,3-bis(*trans*-1-propenyl)carbazole (**1**; 100 mg, 0.405 mmol) and *N*-phenyl-3-(*trans*-1-propenyl)-carbazole (344 mg, 1.21 mmol) in anhydrous dichloromethane (10 mL). After 1.5 min the reaction mixture was quenched with an excess of saturated potassium carbonate in methanol. After the usual two-phase, water/dichloromethane aqueous work-up, the reaction mixture was subjected to column chromatography on silica gel (hexane, hexane/dichloromethane, 9:1, then dichloromethane). Unreacted capping reagent (yield: 62 mg, 14%) was obtained, along with oligomers (yield: 259 mg, 58.3%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.8 – 1.4 (br), 1.6 – 1.9 (br), 1.9 – 2.1 (br), 2.4 – 2.8 (br), 4.2 – 4.4 (br), 4.4 – 4.7 (br), 6.6 – 6.9 (br), 6.9 – 7.8 (br), 7.8 – 8.3 (br); CI LRMS: *m/z* = 495 (2M + 1, where M is the monomer, **1**), 531 (M + M' + 1, where M' is the capping

agent), 567 (2M' + 1), 778 (2M + M' + 1; *major peak*), 779, 814 (M + 2M' + 1; *the parent ion*), 1062 (2M + 2M' + 2), 1309 (3M +2M' + 2), 1345 (2M + 3M' + 2), 1591 (3M + 3M' + 1); EI LRMS: *m/z* = 247 (M; *this is the parent ion*), 283 (M'), 813 (M + 2M'; *major peak*), 1060 (2M + 2M'; *major peak*), 1342 (2M + 3M' – 1); FAB LRMS: *m/z* = 813 (M + 2M'), 1061 (2M + 2M' + 1), 1308 (3M + 2M' + 1), 1591 (3M + 3M' + 1); M_W = 1330, PD = 2.0.

Oligomerization of *N*,3-Bis(*trans*-1-propenyl)carbazole (1) Capped by *N*-(1-*trans*-Propenyl)carbazole

To a stirred solution of tris(4-bromophenyl)aminium hexachloroantimonate (66 mg, 0.08 mmol) in anhydrous dichloromethane (20 mL) at 0 °C under a nitrogen atmosphere was added a solution of *N*,3-bis(*trans*-1-propenyl)carbazole (**1**; 50 mg, 0.202 mmol) and *N*-(*trans*-1-propenyl)carbazole (126 mg, 0.607 mmol) in anhydrous dichloromethane (10 mL). After 1.5 min the reaction mixture was quenched with an excess of saturated potassium carbonate in methanol. Thin layer chromatography indicated that the starting materials had both been completely consumed. After the usual two-phase, water/dichloromethane aqueous work-up, the reaction mixture was subjected to column chromatography on silica gel (hexane, hexane:dichloromethane, 9:1, hexane:dichloromethane, 1:1, then dichloromethane:methanol, 20:1). Two portions of oligomers (yield: 35 mg, 19.9% and 22 mg, 12.5%) and one portion of polymers (yield: 42 mg, 23.9%) were obtained: The ^{1}H NMR of one of the product fractions was not available because of limited solubility; The insoluble fraction had: LRMS: *m/z* = 208 [corresponding to 3-(*trans*-1-propenylcarbazole], 495 (2M + 1), 662 (M + 2M', where M' is the capping agent), 702 (2M + M'), 909 (2M + 2M'). For the soluble fraction: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.8 – 1.3 (br), 1.6 – 1.8 (br), 2.0 – 2.2 (br), 2.6 – 2.8 (br), 3.1 – 3.2 (br), 3.3 – 3.5 (br), 4.2 – 4.4 (br), 4.5 – 4.6 (br), 5.9 – 6.1 (br), 6.1 – 6.3 (br), 6.4 – 6.6 (br), 6.7 – 6.8 (br), 7.0 – 7.5 (br), 7.8 – 8.3 (br); LRMS: *m/z* = 208 ,248 (M), 415 (2M' + 1), 662 (M + 2M' + 1), 702 (2M + M' + 1), 909 (2M + 2M' + 1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.8 – 1.4 (br), 1.6 – 1.8 (br), 1.8 – 2.2 (br), 2.4 – 2.8 (br), 3.2 – 3.6 (br), 4.2 – 4.4 (br), 4.4 – 4.7 (br), 6.6 – 7.0 (br), 7.0 – 7.8 (br), 7.8 – 8.3 (br); Mw = 2.050 (PDI = 3.87), with a minor tail at 95199 (PDI 1.58).

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