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In-chain multi-functionalized polystyrene by living anionic copolymerization with 1,1-bis(4-dimethylaminophenyl)ethylene: Synthesis and effect on the dispersity of carbon black in polymer-based composites

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In-chain multi-functionalized polystyrene possessing definite geminal dimethylamino groups along the polymer backbone, poly(styrene-*co*-1,1-bis(4-dimethylaminophenyl)ethylene) (poly(styrene-*co*-BDADPE)), has been designed and synthesized via living anionic copolymerization of styrene with 1,1-bis(4-dimethylanimophenyl)ethylene in benzene at 50 °C, using *sec*-butyllithium as initiator. The amine functionality was readily controlled by the monomer feed ratio and molecular weight. Compositions of styrene/BDADPE were 9.0–57.9 when ratios of styrene/BDADPE = 0.45–7.79 and Mn = 4.7–15.5 kg/mol. The incorporation of 1,1-bis(4-dimethylanimophenyl)ethylene unit resulted in an increase in glass transition temperature of copolymer and was hindered in the presence of Lewis base. The monomer reactivity ratio for styrene, r_1 = 53.4, was obtained. Such in-chain multi-functionalized polystyrene significantly improved the dispersity of carbon black in the corresponding composites, as verified by SEM observation. This in-chain multi-functionalization of matrix polymer via anionic copolymerization employing 1,1-bis(4-dimethylaminophenyl)ethylene as comonomer provides a facile and effective method to prepare carbon black-based polymer composites with good dispersity.

1. Introduction

1,1-Diphenylethylene, especially its substituted derivatives have been intensely investigated as a general and versatile functionalization adjuvant for anionic synthesis of specialty polymers in terms of function and branched architecture [1–12].

Particularly, the methodology of alkyllithium-initiated copolymerization of substituted 1,1-diphenylethylene derivatives with other appropriate monomers is quite suitable for the synthesis of in-chain multi-functionalized polymers with predictable well-defined functionality and structures. Yuki and Okamoto first investigated the anionic copolymerization of the unsubstituted 1,1-diphenylethylene with styrene [13], ring-substituted styrenes [14–17], isoprene [18], butadiene [19], and 2,3-dimethylbutadiene [20,21]. Quirk et al. further demonstrated the anionic copolymerization of dimethylamino-substituted 1,1-diphenylethylene, i.e., 1-(4-dimethylaminophenyl)-1-phenylethylene, with styrene [22] and butadiene [23]. Then Hayashi [24] described the preparation of styrene-butadiene copolymer with dimethylamino functional groups at both the initiating and terminating chain ends, as well as within the chain in a one-step anionic polymerization. Furthermore, Hutchings and his coworkers [25] reported the monomer sequence distribution in anionic copolymerization of 1,1-diphenylethylene and its derivatives with styrene. Recently, Ding [26] successfully synthesized well-defined in-chain multi-functionalized polymers with a large number of silyl hydride functional groups.

Although the dimethylamino bis-substituted 1,1-diphenylethylene, 1,1-bis(4-dimethylanimophenyl)ethylene (BDADPE), has been investigated as functionalization agent to prepare functional polymers with geminal dimethylamino groups at the chain ends [27,28] and/or within chains [29], few studies have been focused on the in-chain multi-functionalization of polymers via anionic copolymerization employing BDADPE as copolymerizable monomer. Such geminal dimethylamino in-chain multi-functionalized polymers bear twice functional groups than the dimethylamino-substituted analogues with the same content of 1,1-diphenylethylene unit, and thus have extensive application prospect in the fields of sensors, rubber reinforcement, antibacterial agents, catalysts and the like [30–33].

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Carbon black-based polymer composites have attracted increasing interest because of their unique mechanical, electrical, optical, and chemical properties [34–37]. The ultimate performance of these advanced materials depends greatly on the dispersibility of carbon black (CB) in the polymer matrix [38–42]. Hence, interest in the modification with the object of improving the compatibility between fillers and polymer matrix has been intense, including modifications in the bulk or confined to the interface.

One of the most widely used methodologies is the modification of CB and at the same time, various chemical and physical methods for the surface modification of CB have been developed [43], such as plasma treatment [44], ultrasonic treatment [45], chemical-deposit [46], surface oxidation [47,48] reaction with diazonium salts [49], polymer grafting [47,50,51], reaction with silane coupling agents [52], and addition of modifier, e.g., hindered amine light stabilizer LA-57 [32], resorcinol [53], polyvinyl alcohol [54], and oleic acid [55]. In order to make the carbon surface more compatible with the polymer matrix, however, some complicated pretreatments and/or multi steps are required. The compatibility between CB and the polymer matrix can also be improved by enhancing filler–matrix interactions either through covalent bridging, ionic bonds and hydrogen bonds [39,56] or by addition of modifier compatible with immiscible components in these composites [57,58]. The third dramatic method of improving the CB dispersity for polymer-based composites is the functionalization of matrix polymer, i.e., to directly introduce functional groups such as carboxyl and epoxy groups into the matrix polymer which then react with the functional groups present on the carbon surface. For example, Bandyopadhyay and his coworkers [59] reported the better dispersity of surface oxidized CB in carboxylated nitrile rubber matrix with high temperature extrusion in presence of (3-aminopropyl)triethoxysilane. Similarly, Jong investigated the effect of carboxylated styrene-butadiene rubber on the dispersion of CB blended with soy spent flakes [60] and defatted soy flour [61]. In addition, Manna et al. [62] demonstrated the strong interactions between surfaced oxidized CB and epoxidized natural rubber during high-temperature molding. This functionalization of matrix polymer is comparatively simple and flexible; however, little research has been carried out with respect to functionalization of matrix polymer by introducing multiple geminal dimethylamino groups.

In this paper, we report investigations into in-chain multi-functionalization of polystyrene via anionic copolymerization using 1,1-bis(4-dimethylaminophenyl)ethylene as comonomer. Furthermore, we study the impact of such geminal dimethylamino groups along the polystyrene backbone upon the dispersity of CB in the corresponding composites.

2. Experimental

2.1. Materials

The reagents were purchased from Sinopharm Chemical Reagent Company and used as received unless otherwise stated. Benzene was purified by stirring over concentrated sulfuric acid for 2 weeks, followed by overnight drying with ground calcium hydride and distillation. Tetrahydrofuran (THF) was dried by reflux over a Na-benzophenone complex under an argon atmosphere and then distilled. Lewis bases, e.g., anisole, *tert*-butyl methyl ether, tetramethylethylenediamine (TMEDA), and hexamethylphosphoric triamide (HMPTA) were stirred over freshly crushed calcium hydride for 12 h, followed by degassing distillation. *Sec*-butyllithium (*s*-BuLi) was synthesized from Li and *sec*-butyl chloride in benzene, and analyzed using the double titration method with 1,2-dibromoethane [63]. Styrene monomer was purified by dying over CaH_2 followed by vacuum distillation from its *s*-BuLi solution. Methyltriphenylphosphonium bromide (Aldrich, 98%), potassium *tert*-butoxide (Aldrich, 1.0 M solution in THF), and 4,4′-bis(dimethylamino)benzophenone (Aldrich, 98%) were used as received. Carbon black (N550) was purchased from Cabot Company (specific surface area: 40 ± 4 m^2/g, DPB value: 121 ± 5 mL/100 g, average particle size: 40 nm, pour density: 360 ± 40 g/L).

2.2. Measurements

^1H NMR (5 wt%, $CDCl_3$) spectra were recorded on a Bruker AvanceII 400M NMR spectrometer with $(CH_3)_4Si$ (tetramethylsilane) as the internal standard. Size exclusion chromatographic (SEC) analyses of the copolymers were performed on a Waters HPLC component system (2414 refractive index detector) at a flow rate of 1.0 mL/min in THF at 30 °C after calibration using polystyrene standard polymers. Glass transition temperatures (T_g) of the polymers were measured under nitrogen atmosphere using a TA Instruments Universal Analysis 2000 differential scanning calorimeter (DSC) at a heating rate of 10.0 °C/min. Sample sizes were 10 mg and investigated under nitrogen. Scanning electronic microscopy (SEM) observations were carried out using a FEI Quanta 200F at an acceleration voltage of 20 kV. Samples were fractured under ambient condition, and the fracture surfaces were covered with a layer of gold by sputtering treatment before SEM observation. Contents of bound polymer were determined by extracting unbound polymer with toluene for 3 days at room temperature and drying in a vacuum oven to a constant weight. Weights of the samples before and after the extraction were measured and the bound polymer contents were calculated [64].

2.3. Synthesis of 1,1-bis(4-dimethylaminophenyl)ethylene

The synthesis of BDADPE was conducted by the classic Wittig reaction using 4,4′-bis(dimethylamino)benzophenone as substrate under an argon atmosphere (described in detail by Hirao [29]). Typically, methyltriphenylphosphonium bromide (45.58 g, 127.6 mmol) and freshly distilled THF (500 mL) were added into a round bottom flask equipped with a reflux condenser and a magnetic bar. Potassium *tert*-butoxide (138.4 mL of a 1.0 M solution in THF, 138.4 mmol) was then added dropwise to the reaction flask via constant pressure funnel. The reaction mixture was stirred for 2 h at 0 °C. Then the solution of 4,4′-bis(dimethylamino)benzophenone (21.4 g, 79.75 mmol) in dry THF (690 mL) was dropped to the reaction mixture via constant pressure funnel at 0 °C. The orange–brown reaction mixture was heated to reflux for 7 h with stirring and then quenched with distilled water. The resultant mixture was extracted with ether three times. Such ethereal layer was washed with aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution and then dried over $MgSO_4$. After filtration, the ethereal layer was poured into hexane to precipitate triphenylphosphine oxide. Flash column chromatography (petroleum ether/ethyl acetate 2:1 v/v) gave BDADPE in 92% yield (19.52 g, 73.37 mmol) and $R_f = 0.76$. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.96 (s, 12H, $2 \times N(CH_3)_2$), 5.19 (s, 2H, $CH_2 = C$), 6.68–6.70 (d, 4H, aromatic proton *ortho* to $N(CH_3)_2$), 7.25-7.28 (d, 4H, aromatic proton *meta* to $N(CH_3)_2$).

2.4. Synthesis of poly(styrene-co-1,1-bis(4-dimethylaminophenyl)ethylene)

Copolymerizations were carried out at 50 °C in ampoule under an argon atmosphere. Styrene and 1,1-bis(4-dimethylaminophenyl)ethylene were first dissolved in benzene in the same ampoule with or without addition of the required Lewis base. Samples were then prepared by adding a solution of *s*-BuLi to the comonomer solution. The copolymerization was proceeding under stirring for 24 h and then quenched with degassed isopropanol. The resultant copolymers were precipitated into excess methanol three times to remove unreacted BDADPE from the polymer and then dried in a vacuum oven to constant weight.

2.5. Preparation of CB/poly(styrene-co-1,1-bis(4-dimethylaminophenyl)ethylene) composites

The composites were fabricated by the solution method. First, the copolymer powders were dissolved in THF under stirring for 2 h at ambient temperature to obtain solutions at 0.033 g/mL. In the second step, CB pellets were introduced into these solutions with stirring for 6 h to obtain homogeneous solutions with a CB/polymer weight ratio of about 5.22/94.78. Then the CB/polymer solutions were deposited onto glass slides cleaned in methanol and THF was slowly evaporated at 30–40 °C.

3. Results and discussion

3.1. Copolymerization of styrene and 1,1-bis(4-dimethylaminophenyl)ethylene

3.1.1. Preparation of styrene-co-BDADPE copolymers

The copolymerization of styrene and excess BDADPE was initiated by *s*-BuLi in benzene at 50 °C, as shown in Scheme 1. To explicitly characterize the structure, the product was purified by precipitating into excess methanol three times to remove the unreacted BDADPE from the polymer.

The products were collected and characterized by ^{1}H NMR spectrometry. As seen in the ^{1}H NMR spectra in Fig. 1, the complete disappearance of the peak around δ 5.19 ppm simultaneously with the appearance of the peak about δ 2.6–3.0 ppm is unambiguous evidence that the crossover reaction take place by nucleophilic attack of poly(styryl)lithium on the double bond of BDADPE monomer. And the dimethylamino protons at $\delta = 2.6–3.0$ ppm show splittings ascribed to different diastereomeric arrangements of the functional groups as observed previously [65].

The purified product was further analyzed by SEC using polystyrene standards for calibration. The molecular weights and molecular weight distributions are listed in Table 1. Somewhat broader molecular weight distributions were obtained for these purified products compared to homopolystyrene because of the slower rate of crossover relative to propagation [66]. The SEC overlay of purified product and polystyrene with the same number of styrene unit is shown in Fig. 2. The trace of the purified product shows a shift to smaller retention volume in comparison with that of polystyrene.

Therefore, the above evidence has explicitly verified the chemical structure of styrene-*co*-BDADPE copolymer.

3.1.2. Copolymer compositions

The amine functionality, F, corresponding to the number of geminal dimethylamino groups per polymer chain, was calculated from the ^{1}H NMR spectra of the copolymers using Eqs. (1) and (2):

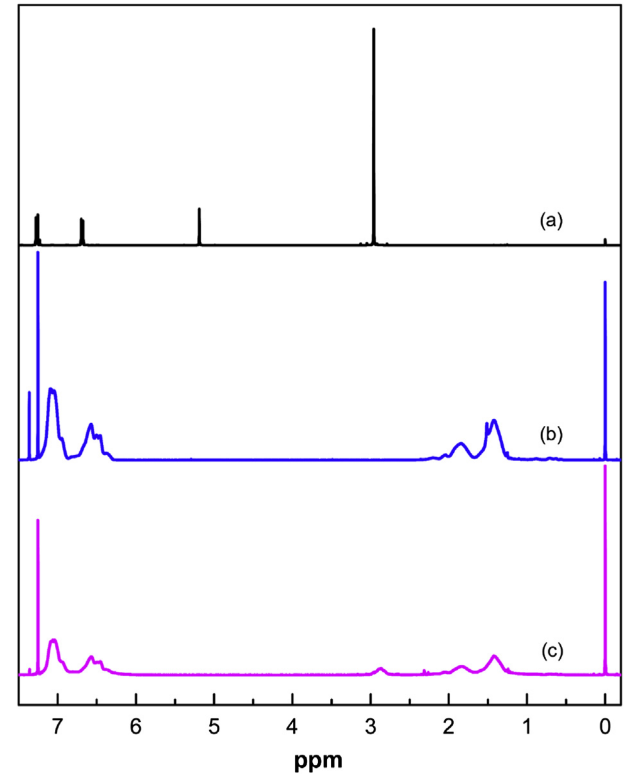


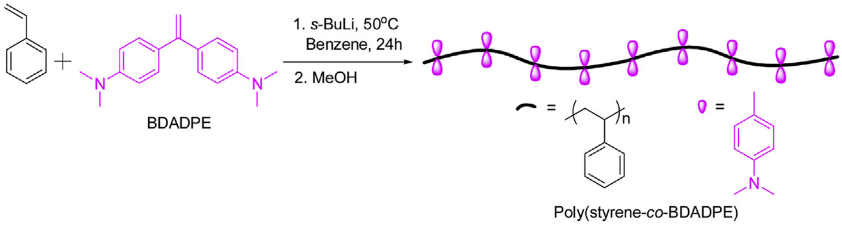
Fig. 1. ^{1}H NMR spectra (CDCl$_3$) of BDADPE (a), polystyrene (b), and poly(styrene-*co*-BDADPE) (c).

$$\frac{12n_2}{8n_2+5n_1} = \frac{\text{Area}[-\text{N}(\text{CH}_3)_2]}{\text{Area}[\text{aromatic region}]} \tag{1}$$

$$M_1n_1 + M_2n_2 = \overline{M\text{n}} \tag{2}$$

where n_i refers to the average number of monomer i unit incorporated into the copolymer, M_i and Mn are the molecular weight of monomer i and the number average molecular weight of the copolymer, respectively. The copolymer compositions were also calculated from ^{1}H NMR integration ratios.

The functionalities and copolymer compositions are summarized in Table 1 and shown in Fig. 3. The molar content of geminal dimethylamino groups along the polymer chain increased from 1.7% to 10.0% as the monomer feed molar ratio decreased from 7.79 to 0.45 with Mn in range of 4.7–15.5 kg/mol. This is in accord with the general trend of styrene anionic copolymerization with 1,1-diphenylethylene [13] and its amino-substituted derivative [22]. Thus, the number of geminal dimethylamino groups along polystyrene backbone could be controlled by the monomer feed ratio and the molecular weight.



Scheme 1. Synthesis of in-chain multi-functionalized polystyrene using BDADPE as comonomer.

Table 1
Monomer feed ratio, composition and glass transition temperature data for styrene (M_1)-BDADPE (M_2) copolymers.

Sample	$[M_1]_0/[M_2]_0$[a]	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn	$[M_1]/[M_2]$[b]	F[c]	T_g (°C)
1[d]	–	11.6	12.9	1.11	–	–	89.9
2	0.45	4.7	5.6	1.19	9.0	3.9	106.6
3	0.56	7.6	9.2	1.21	11.0	5.4	104.3
4	0.79	10.3	12.3	1.19	13.6	6.1	103.9
5	2.30	15.5	19.3	1.25	26.5	5.1	101.8
6	2.40	12.4	15.1	1.22	27.2	4.0	99.7
7	3.70	9.9	12.2	1.23	37.6	2.4	97.3
8	4.76	12.1	14.5	1.20	41.2	2.7	93.2
9	7.79	13.6	14.7	1.08	57.9	2.2	93.0

[a] Molar concentration ratio of the two monomers at the beginning of polymerization, which is the same as the monomer molar feed ratio.

[b] Copolymer composition, i.e., the molar ratio of the two monomer units in the copolymer, calculated from the ^{1}H NMR spectra of the copolymers using Eqs. (1) and (2).

[c] Amine functionality corresponding to the number of geminal dimethylamino groups per polymer chain calculated from the ^{1}H NMR spectra of the copolymers using Eqs. (1) and (2).

[d] Homopolystyrene.

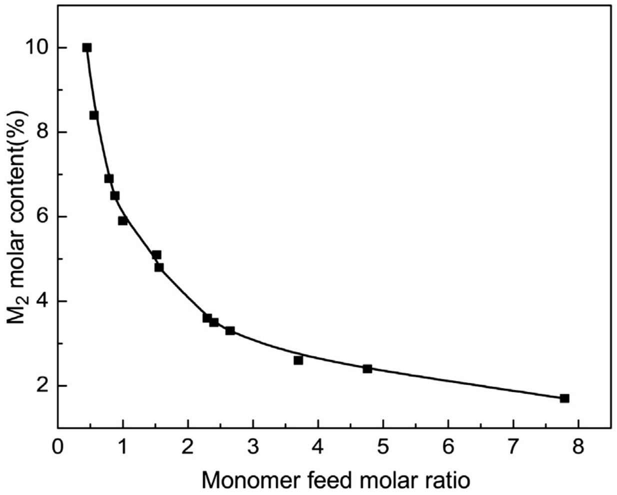


Fig. 3. Molar content of geminal dimethylamino groups in styrene-*co*-BDADPE copolymers as a function of the monomer feed molar ratio of styrene to BDADPE.

On the basis of above results, it is concluded that this in-chain multi-functionalization procedure via anionic copolymerization employing BDADPE as comonomer can be utilized to prepare functionalized polymers with multiple geminal dimethylamino groups along the polymer backbone.

3.1.3. *Thermal properties of copolymers*

The copolymers possessing multiple geminal dimethylamino groups were tested for their thermal properties by DSC. The relevant data is collected in Table 1 and the corresponding DSC curves are shown in Fig. 4.

It appears that each random copolymer had only one glass transition temperature, as expected. Furthermore, an increasing trend in T_g from 89.9 °C to 106.6 °C was observed as the decreasing value of monomer feed ratio. Such an increase in T_g is attributed to the increasing molar content of polar geminal dimethylamino diphenyl functional groups incorporated into the polymer which increase the polar interaction between the polymer chains. It is interesting to note that the incorporation of modest amounts of 1,1-bis(4-dimethylaminophenyl)ethylene units (10.0 mol-%) resulted in relatively large increase in T_g of the resulting copolymer (Sample 2 in Table 1; $Mn = 4.7$ kg/mol; $T_g = 106.6$ °C), more than 24.6 °C higher than homopolystyrene with the same molecular weight [67]. Relative to dimethylamino-substituted analogues [22], the geminal dimethylamino-substituted copolymers obtained in the present study exhibited lower T_g values with the similar copolymer composition and *M*n values. This may be due to the decrease of the dipole moment which results from the symmetrical dimethylamino bis-substitution in the phenyl rings of 1,1-diphenylethylene molecule.

The characterization by thermal analysis indicates that copolymerization of styrene with BDADPE is an effective means of increasing the glass transition temperature as well as increasing the polar interaction between the polymer chains.

3.1.4. *Monomer reactivity ratio for styrene*

If it is assumed that the styrene monomer is completely consumed at the end of the polymerization, the Mayo-Lewis copolymerization equation [68] for our system takes the integrated form as shown in Eq. (3):

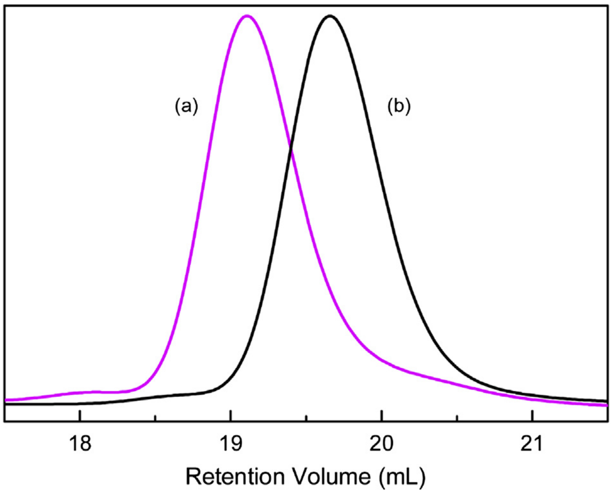


Fig. 2. SEC overlay of poly(styrene-*co*-BDADPE) (a) and polystyrene with the same number of styrene unit (b).

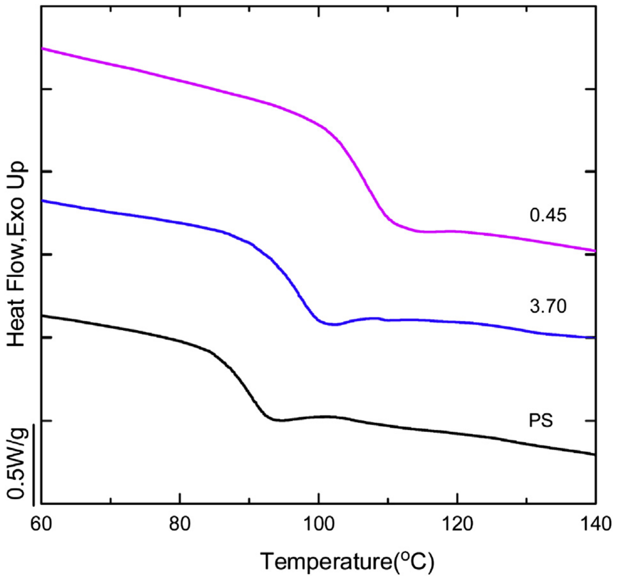


Fig. 4. DSC curves of poly(styrene-*co*-BDADPE). Each bracket indicates the corresponding monomer feed ratio.

$$\ln\frac{[M_2]}{[M_2]_0}+\frac{1}{r_1-1}\ln\left\{\frac{[M_1]_0}{[M_2]_0}(r_1-1)+1\right\}=0 \tag{3}$$

where $[M_1]_0/[M_2]_0$ is known from the monomer feed and $[M_2]/[M_2]_0$ can be determined from the final copolymer composition. Thus the value of r_1 can be solved by trial and error from Eq. (3).

When styrene was copolymerized with BDADPE in benzene at 50 °C with *s*-BuLi as initiator, the values of monomer reactivity ratio for styrene, r_1, are listed in Table 2. The average value of r_1 was calculated to be 53.4. This means that styrene is 53.4 times more reactive than BDADPE towards the poly(styryl)lithium anion. In the previous studies, r_1 is reported to be 5.6 for styrene in copolymerization with 1-(4-dimethylaminophenyl)-1-phenylethylene in benzene at 25 °C [22]. These results are consistent, since the addition reaction of 1,1-diphenylethylene derivatives to poly(styryl)lithium is accelerated by electron-withdrawing substituents and retarded by electron-donating substituents in the phenyl rings [69]. In our system both phenyl groups of 1,1-diphenylethylene molecule were equally substituted by strong electron-donating dimethylamino groups [70]. Thus, the crossover reaction rate of poly(styryl)lithium to BDADPE is much less than that of poly(styryl) lithium to 1-(4-dimethylaminophenyl)-1-phenylethylene. Therefore, the monomer reactivity ratio, r_1 ($r_1 = k_{11}/k_{12}$), is expected to be much larger in copolymerization with BDADPE than that with 1-(4-dimethylaminophenyl)-1-phenylethylene.

The Hammett relationship for the addition reaction of poly(styryl)lithium to the 1,1-diphenylethylene system can be described by Eq. (4):

$$\log\frac{k_{12}}{k_{12}^0}=\rho\sigma \tag{4}$$

where $\rho = +1.8$ [69], k_{12}^0 and k_{12} are the crossover reaction rates of poly(styryl)lithium to 1,1-diphenylethylene and a substituted 1,1-diphenylethylene, respectively.while

$$\frac{r_1^0}{r_1}=\frac{k_{11}/k_{12}^0}{k_{11}/k_{12}}=\frac{k_{12}}{k_{12}^0} \tag{5}$$

where k_{11} is the homopropagation of styrene. Upon substituting the value of k_{12}/k_{12}^0 from Eq. (5) into Eq. (4), then Eq. (6) is obtained:

$$\log\frac{r_1^0}{r_1}=\rho\sigma \tag{6}$$

A σ value of −1.04 for the geminal para-dimethylamino substituent could be calculated from Eq. (6) using $r_1^0 = 0.71$ [13], $r_1 = 53.7$, and $\rho = +1.8$ [69]. Representative literature values of σ for the *para*-dimethylamino substituent are −0.44, −0.71, −0.83 [70–72], and −0.5 [22]. The substituent constant (σ) obtained in this work is twice the normal σ constant reported by Quirk [22], which is consistent with expectations in the literature [73]. With a substituent constant of −1.04, the geminal dimethylamino groups strongly retard the nucleophilic attack by a carbanion on the double bond of the BDADPE monomer in comparison to 1,1-diphenylethylene and 1-(4-dimethylaminophenyl)-1-phenylethylene. Thus the much larger value of the monomer reactivity ratio for styrene in copolymerization with BDADPE is in accord with expectations based on the electronic properties of the geminal dimethylamino groups.

Table 2
Monomer reactivity ratio for styrene in copolymerization with BDADPE.

$[M_1]_0/[M_2]_0$	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn	$[M_1]/[M_2]$	F	$[M_2]$[a] (%)	r_1[b]
1.52	15.3	19.1	1.25	18.6	6.9	5.1	52.2
1.56	17.3	21.8	1.26	20.0	7.4	4.8	55.8
2.30	15.5	19.3	1.25	26.5	5.1	3.6	54.0
2.40	12.4	15.1	1.22	27.2	4.0	3.5	53.4
2.65	14.3	17.2	1.20	29.5	4.3	3.3	53.5
3.70	9.9	12.2	1.24	37.6	2.4	2.6	51.5

Conditions: reaction time = 24 h at 50 °C.

[a] Molar content of the geminal dimethylamino groups of styrene-*co*-BDADPE copolymers.

[b] Calculated according Eq. (3).

Table 3
Effect of Lewis base on composition of styrene-BDADPE copolymers.

Lewis base	n(LB/*s*-BuLi)	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn	$[M_1]/[M_2]$	F	$[M_2]$ (%)
–	0.0	14.3	17.2	1.20	29.5	4.3	3.3
Anisole	14.0	22.5	28.3	1.26	36.7	5.5	2.7
tert-Butyl Methyl Ether	5.3	27.1	32.5	1.20	98.0	2.6	1.0
THF	2.5	18.4	20.9	1.14	60.5	2.8	1.6
TMEDA	0.1	9.6	11.6	1.21	45.2	1.9	2.2
HMPTA	0.1	11.8	13.2	1.12	68.8	1.6	1.4

Conditions: $[M_1]_0/[M_2]_0 = 2.65$; reaction time = 24 h at 50 °C.

3.1.5. *Effect of Lewis base*

Because of such unfavorable monomer reactivity ratio, it was anticipated that the addition of Lewis base would be necessary to promote significant incorporation of BDADPE units. Therefore, the effect of several Lewis base on the final copolymer composition was investigated. The copolymers were collected for ^{1}H NMR and SEC analyses.

The results are presented in Table 3. When styrene was copolymerized with BDADPE in the presence of Lewis base ranging in polarity from weak anisole to mild THF and further to strong HMPTA, less BDADPE units were incorporated into the copolymers in the molar ratio range studied here. This is the opposite of that for the butadiene-1-(4-dimethylaminophenyl)-1-phenylethylene system [23]. It would be reasonable to expect that the complex, formed by Lewis base and living polymer chain, would tend to hinder sterically approach of the coming BDADPE monomer relative to attach at the hindered terminal chain end in absence of Lewis base. This could explain the decrease in incorporation of BDADPE unit in the presence of Lewis base.

3.2. *CB/poly(styrene-co-BDADPE) composites*

3.2.1. *Composite morphologies*

In order to investigate the effect of such incorporated geminal dimethylamino functional groups on the dispersity of CB in the corresponding polymer matrix, three composites, C1, C2 and C3, with strong deviations in dimethylamino group content but almost identical in carbon black content, were prepared. The composite formulation data is given in Table 4. SEM was used to study the

Table 4
Composite formulation with varied dimethylamino group content and similar CB content.

Composite	CB content (wt%)	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn	$[M_1]/[M_2]$	F	$[M_2]$ (%)	Bound polymer content (%)
1	5.22	11.6	12.9	1.11	–	–	–	2.1
2	5.22	9.9	12.2	1.23	37.6	2.4	2.6	6.5
3	5.22	14.0	16.5	1.18	10.9	10.0	8.4	8.6

fracture surface morphology of CB/in-chain multi-functionalized polystyrene composites.

As shown in Fig. 5, distinct morphologies were observed for these three composites. For example, when dispersed in pure PS matrix, CB particle domain had a very broad distribution and there was an amount of large carbon agglomerates in dimension varying from 2 to 12 μm. This result may be due to the weak filler–matrix interaction consisting of Van Der Waals types of forces. As for functionalized polystyrene-based composites, Composite 2, with 2.6 mol-% geminal dimethylamino groups, contained much less carbon agglomerates of which the domain size decreased sharply to 1–2 μm. A similar trend was discovered for Composite 3, with the molar content of geminal dimethylamino groups further increasing to 8.4%, where the composite contained uniformly dispersed CB aggregates.

It is evident that the incorporation of geminal dimethylamino groups into the matrix polystyrene backbone changes the morphology of the corresponding CB-based composite. Thus, the improvement in dispersity of CB should stem from the strong interaction between such geminal dimethyamino groups and CB only. This is not a usual interaction formation process. An explanation for this strong interaction formation is attempted in the next section.

3.2.2. *Mechanism of strong interaction formation*

Here we attempt to propose a strong interaction mechanism, i.e., ionic bonds and hydrogen bonds, for the improvement in dispersion of CB in such amine-functionalized polystyrene as illustrated in Scheme 2.

These SEM micrographs reveal more uniformly dispersed CB in geminal dimethylamine-functionalized polystyrene matrixes compared with that in unfunctionalized matrix. As unfunctionalized PS/CB composite is compounded under similar processing condition as the functionalized polystyrene/CB composites, such improvement in dispersity of CB is ascribed to the introduction of multiple geminal dimethylamino groups along the polystyrene backbone which interact with functional groups present on CB surface to form strong filler–matrix interaction. Therefore, there are less carbon agglomerates and meanwhile the domain size of CB agglomerates is remarkably decreased, as is indicated in the illustration of Fig. 6 (a) and (b). In addition, the degree of improvement in dispersity of CB greatly depends on the content of geminal dimethylamino groups of the matrix polymer. It is worth mentioning here that, with the amine functionality further increasing to 8.4 mol-%, Composite 3 contains uniformly dispersed CB aggregates (Fig. 6 (c)).

Several works of functionalization of matrix polymer in the literature employed carboxyl and epoxy functions to interact with functional groups present on the modified CB surface, which only form hydrogen bonds [59–62]. By means of functionalization of matrix polystyrene by incorporating multiple geminal dimethylamino groups we are quite confident to the presumption that, in addition to the formation of hydrogen bonds, such *tert*-amino groups also should react with intrinsic acidic functional groups present on the carbon surface, and give rise to the formation of high-energy ionic bonds at ambient condition.

Scheme 2 suggests the strong interaction between CB and in-chain multi-functionalized polystyrene, illustrating the role of geminal dimethylamino groups in the filler–matrix interaction. It is proposed that the geminal dimethylamino groups along the polymer backbone interact with acidic groups on the surface of CB, such as carboxyl, phenol, and hydroxyl, to form ionic bonds as well as hydrogen bonds. These high-energy bonds reduce the extent of CB agglomerate formation and enhance the filler–matrix interaction. As seen in Table 4, the bound polymer content in CB-filled polymer composites increased as the content of geminal dimethylamino groups of the matrix polymer increased, and this is in accord with expectation based on the strong interaction mechanism presented above. Therefore, this strong interaction results in good compatibility of CB and polymer matrix and thus allows the CB better dispersion and homogeneity than that in pure PS matrix. The effect of such incorporated geminal dimethylamnio groups on the CB

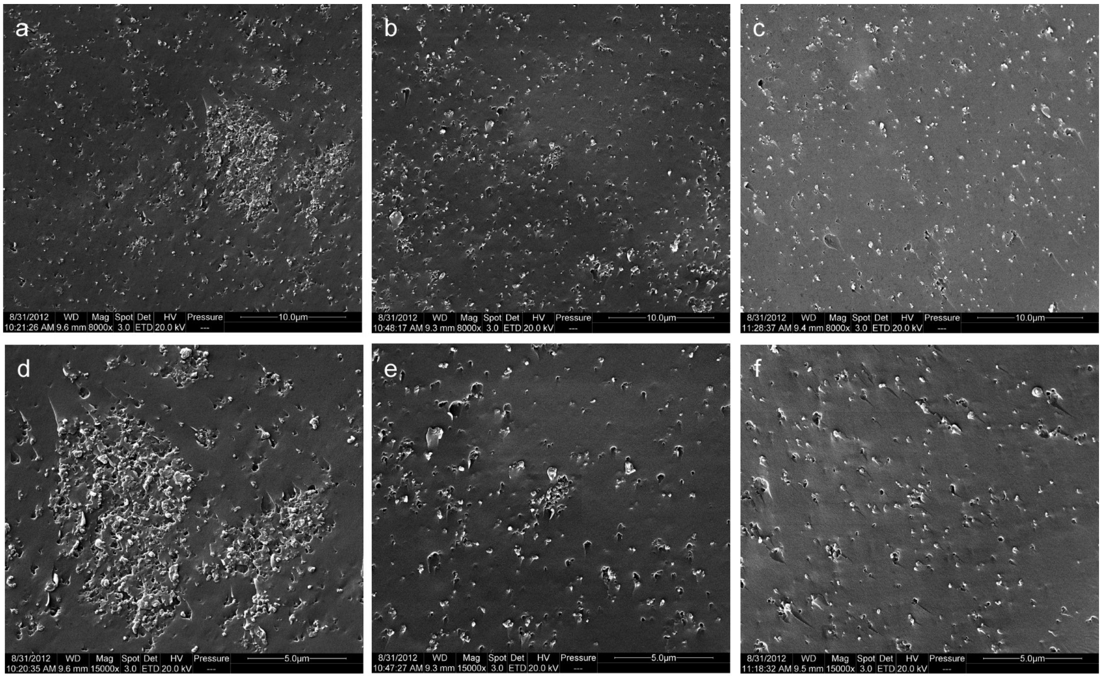
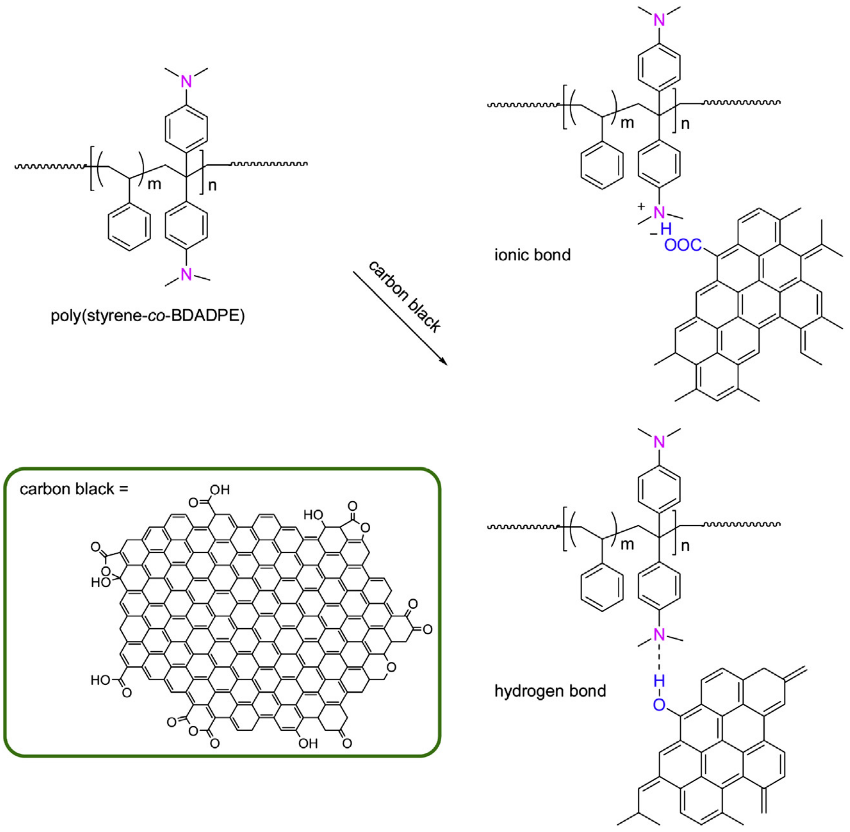


Fig. 5. SEM micrographs of fracture surface of in-chain multi-functionalized polystyrene filled with 5.22 wt% CB and the molar content of geminal dimethylamino groups: 0 for Composite 1 (a and d), 2.6% for Composite 2 (b and e) and 8.4% for Composite 3 (c and f).



Scheme 2. Proposed mechanism for the formation of ionic bonds and hydrogen bonds between CB and in-chain multi-functionalized polystyrene with geminal dimethylamino groups.

dispersion is evident in the light of the SEM studies as shown in Fig. 5.

In summary, functionalization of matrix polymer by introducing multiple geminal dimthylamino groups into polymer backbone effectively improves the dispersity of CB in polymer-based composites. It should be noted that this paper has studied only the effect of *tert*-amino groups on CB dispersity. In the case of employing primary amine groups, covalent bonds, i.e., amido linkage should be formed between CB and polymer matrix upon application of heating, which should be quite favorable for filler–matrix interaction. However, this problem could be solved by using the 1,1-bis(4-aminophenyl)ethylene as comonomer in conjunction with functional group protection.

Compared with traditional complicated and lengthy methods, the method developed in this work can be conveniently applied especially with regard to the rubber reinforcement [35], CB-filled elastomers and high-performance automotive tires [74], and sensor arrays [75]. Potential practical applications of this geminal

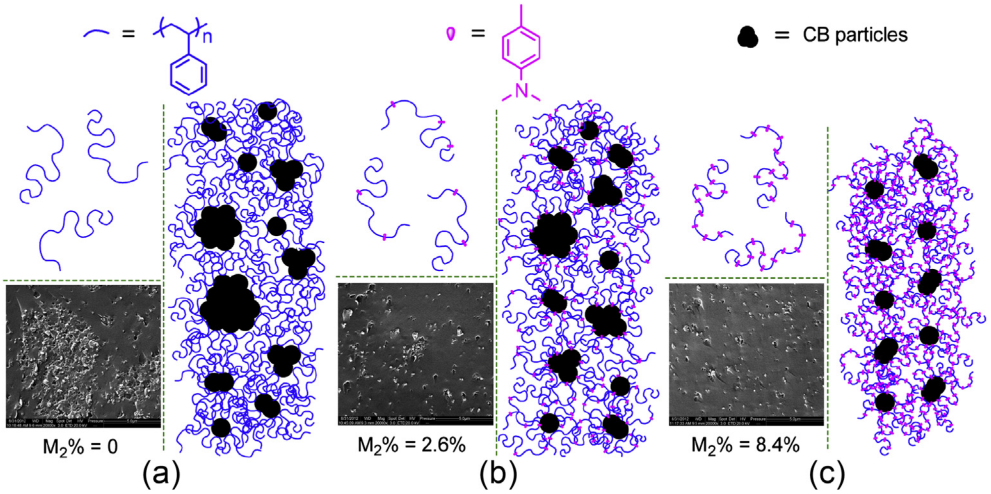


Fig. 6. Representation of the structure models of CB-based polymer composites as a function of the geminal dimethylamino group content $M_2\%$: (a) large CB agglomerates coexisting with aggregates, (b) small and less CB agglomerates along with aggregates, and (c) CB aggregates.

dimethylamino in-chain multi-functionalized polymer are under investigation.

4. Conclusions

Based on the above results, it is concluded that the number of geminal dimethylamino groups along the polystyrene backbone is definitely controlled by the monomer feed ratio and the molecular weight via anionic copolymerization with 1,1-bis(4-dimethylphenyl)ethylene; therefore, in-chain multi-functionalized polymers can be rationally designed and practically synthesized according to the application of interest. Furthermore, the SEM studies revealed great improvement in terms of dispersity of CB in such multiple geminal dimthylamine-functionalized polystyrene matrix. The method developed in this work provides a facile and controllable route to prepare the polymer-based composites containing finely dispersed CB, and this method is versatile because the geminal dimethylamine in-chain multi-functionalized polymer constructs a platform for the functionalization of a substantial number of other materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.04.011.

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