Polycarbosilane-modified styrene-based polymers with ultra-low dielectric constant, greatly enhanced mechanical strength and thermal stability

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ABSTRACT

Ultra-low dielectric constant (ε) materials have aroused much attention in recent years. In this work, taking styrene polymers as an example which have low ε but poor mechanical strength, we find a hopeful way to fulfill the task via graft copolymerization. The graft copolymerization was conducted by a reaction of silacyclobutene pendant groups on polystyrene polymer with disilacycobutene (DSCB) via ring-opening reaction, forming polystyrene with polycarbosilane structures on side chains. The curing of graft polystyrene via reaction of BCB results in the polycarbosilane-modified styrene resins. Cured graft polystyrene exhibited T_d around 460 °C, which is greatly higher than unmodified styrene resins. Nanoindentation measurement showed that as compared with unmodified styrene resins, the modulus of cured graft polystyrene was greatly increased from 0.18 to 8.1 GPa. More attractively, the graft polystyrenes also exhibit significantly low ε. The lowest value for as-prepared graft polystyrenes reaches to ~1.85, thus providing a new strategy to achieve ultra-low ε via grafting technique.

1. Introduction

Low dielectric (ε) materials have been found wide application in microelectronic packaging and electromagnetic wave transmitting [1–5]. Particularly, with the rapid development of microelectronic and telecommunication industries, ultra-low ε materials have aroused much attention owing to their outstanding performance on decreasing signal delay and increasing speed. Currently, there are mainly two routes to decrease ε for polymeric materials. A large number of polymers have been developed for these applications, such as benzocyclobutene (BCB) resins [6], polynorbornenes [7], poly(naphthylene)s [8] and fluoropolymers [3,9]. However, it can be discovered that almost all of these polymers have ε over 2.2 if pores are not introduced, implying that chemical structure design alone is not enough to achieve ultra-low ε.

Up to date, incorporating pores in materials have demonstrated a powerful tool to realize ultra-low ε [10–13]. Nevertheless, it will possibly sacrifice mechanical strength and thermal stability. Apart from this, the size of pores must be lower than that of feature size. Thus, microporous and mesoporous structures are suitable for ultra-low-ε materials [14–16]. In recent years, design of molecular free volume has aroused much attention to reduce ε [17–19]. Side chain which is large as well as of high rigidity was generally designed to attain large

molecular free volume and demonstrated success to in attaining low or ultra-low ε. However, all of these studies have focused on small molecular side chain. No study was reported on low-ε polymers with grafted structure. In theory, as is compared with small molecular side chains or directly cross-linking, the introduction of graft macromolecular chain may at least have following advantages. First, it may enlarge molecular free volume owing to the increased inter-chain distance, thus making it more powerful to reduce ε. Second, the property of pristine polymer will be greatly enhanced by graft polymers. However, for introducing small molecular side chains or directly cross-linking, the property is enhanced just in a limited degree.

Styrene-based polymers, which are a kind of industrialized polymers prepared by free radical polymerization of styrene monomers, have shown potential application as low-ε materials. Styrene-based polymers have low ε because they are mainly constructed by C−C and C−H bonds, typically, the ε of polystyrene is around 2.7 [20]. Our group recently reported two kinds of styrene copolymers, poly (4-silylvinyl-benzocyclobutene-r-styrene) and poly (4-vinylbenzocyclobutene-r-styrene), which have the ε of around 2.6 and 2.4, respectively [21]. So et al. reported the preparation of poly (styrene-co-4-vinylbenzocyclo-butene) and investigated its potential use for microelectronic applications [22]. However, there is still not any report on ultra-low ε styrene-

based polymers. Besides, the application of styrene-based polymers is also limited by their unsatisfactory thermal stability and mechanical strength.

In this study, we attempt to integrate a polymeric structure in side chain of styrene resins and to evaluate its effect on the performance of styrene resins. The polymer is required to combine outstanding mechanical/thermal with low-ε properties. Amongst a large number of polymers, we find that poly (carbosilane)s (PCSs) have been a few of high performance materials meeting the above requirement. PCSs are a family of hybridized polymers [23], which can be prepared by a series of reliable methods, including polycondensation, hydrosilylation reaction, ring-opening polymerization (ROP), etc. [24]. Our group have also prepared a series of PCSs and demonstrated their outstanding low ε property and high thermal stability [21b,25]. However, grafting polycarbosilane on polymers is still a challenging task. Herein, we reported a method to create polycarbosilane-grafted polystyrenes by a copolymerization of silacyclobutane groups on polystyrene with disilacyclobutene. These polymers were further cured via the reaction of benzocyclobutene (BCB) pendant groups to form polycarbosilane-modified styrene resins. Three polymers were prepared via tailoring the mole ratio of disilacyclobutene to silacyclobutene groups. The chemical structures, curing, thermal stability, mechanical strength and dielectric constant of PCS-PSs were investigated in detail.

2. Experimental

2.1. Materials

All manipulations involving air-sensitive materials were carried out in oven-dried glassware under nitrogen. 1,3-dimethyl-1,3-dibenzocyclobutene-1,3-disilacyclobutane (DMDBDC) and copolymer of styrene, 4-vinylbenzocyclobutene (4-VBCB) and 1-methyl-1-(4-vinylphenyl) silacyclobutane (1-MVPSCB) were synthesized by our group [21b,25]. Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Alfa Aesar Company. Tetrahydrofuran (THF) and toluene were distilled over sodium-benzophenone before use. Styrene was distilled over calcium hydride in prior to use.

2.2. Synthesis of 4-vinylbenzocyclobutene (M1)

4-VBCB was synthesized according to the reported method [21b]. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.26 (d, 1H, ArH), 7.20 (s, 1H, ArH), 7.04 (d, 1H, ArH), 6.74 (dd, 1H, CH), 5.70 (d, 1H, CH$_2$), 5.20 (d, 1H, CH$_2$), 3.19 (s, 4H, CH$_2$). HRMS (ESI) m/z calcd for $C_{10}H_{10}$ (M + H)$^+$ 131, found 131.

2.3. Synthesis of 1-methyl-1-(4-vinylphenyl) silacyclobutane (M2)

In a 100 mL round-bottom flask, 1,2-dibromoethane (3 drops), magnesium (1.90 g, 80 mmol), and dry THF (5 mL) were added and stirred at ambient temperature for 30 min under nitrogen. Then 3-chloropropylmethyldichlorosilane (9.50 mL, 60 mmol) in THF (45 mL) was added dropwise over a period of 15 min and the reaction mixture was heated to 50 °C for another 2 h. In another flask, magnesium (1.44 g, 60 mmol) and a grain of iodine were added. Then 4-Bromostyrene (9.15 g, 50 mmol) in 30 mL of dry THF was slowly added dropwise over a period of 2 h under nitrogen atmosphere. The reaction mixture was heated to 50 °C and stirred continuously for 1 h. Resulted solution was added to the first flask. The reaction temperature was elevated to 50 °C and kept overnight. Then the solution was poured into 1 M aq. HCl and extracted with hexane. The organic layer was washed twice with water and dried over anhydrous sodium sulfate. After removing the solvents by rotary evaporation, the residual liquid was purified by column chromatography (petroleum ether) to give a colorless liquid (6.02 g, 64%); ^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.58 (d, J = 19.5 Hz, 2H, ArH), 7.43 (d, J = 16.8 Hz, 2H, ArH), 6.72 (d, 1H,

−CH=C), 5.78 (d, J = 34.7 Hz, 1H, −C=CH$_2$), 5.28 (m, 1H, −C=CH$_2$), 2.19 (m, 2H, −C−CH$_2$−C−), 1.31 (m, 2H, −Si−C−C−CH$_2$−), 1.16 (m, 2H, −Si−CH$_2$−C−C−), 0.55 (s, 3H, Si−CH$_3$). HRMS (ESI) m/z calcd for $C_{12}H_{16}Si$ (M + H)$^+$ 189, found 189.

2.4. Synthesis of 1,3-dimethyl-1,3-dibenzocyclobutene-1,3-disilacyclobutane (M3)

In a 100 mL round-bottom flask, 1,2-dibromoethane (0.30 mL), magnesium (1.64 g, 68 mmol), and dry THF (5 mL) were added and stirred at ambient temperature for 30 min under nitrogen. Then (chloromethyl)methylisoproxychlorosilane (10.05 g, 57 mmol) in THF (26 mL) was added dropwise over a period of 15 min and the reaction mixture was heated to 50 °C for another 2 h. In another flask, magnesium (1.64 g, 68 mmol) and a grain of iodine were added. Then 4-bromobenzocyclobutene (9.86 g, 57 mmol) in 27 mL of dry THF was slowly added dropwise over a period of 2 h under nitrogen atmosphere. The reaction mixture was heated to 50 °C and stirred continuously for 1 h. Resulted solution was added to the first flask. The reaction temperature was elevated to 50 °C and kept overnight. Then the solution was poured into 1 M aq. HCl and extracted with hexane. The organic layer was washed twice with water and dried over anhydrous sodium sulfate. After concentrating by rotary evaporation, the product was purified by column chromatography using petroleum ether as elution to give colorless liquid (29 mmol, 9.3 g) in 51% yield. ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.70 (d, 1H, ArH), 7.63 (d, 1H, ArH), 7.56 (d, 1H, ArH), 7.47 (s, 1H, ArH), 7.29 (d, 1H, ArH), 7.24 (d, 1H, ArH), 3.41–3.36 (m, 8H, −CH$_2$CH$_2$−), 0.53 (d, 6H, Si−CH$_3$), 0.42 (s, 4H, SiCH$_2$Si). HRMS (ESI) m/z calcd for $C_{20}H_{24}Si_2$ (M + H)$^+$ 321, found 321.

2.5. Synthesis of benzocyclobutene-attached polycarbosilane (P1)

In a typical experiment, M3 (1.90 g; 6 mmol) and H_2PtCl_6 (100 μL; 0.025 M in THF) were dissolved in 4 mL of THF. The polymerization was conducted at 100 °C for 24 h. After cooled to room temperature, the solution was poured into a large excess of methanol. The precipitation was repeated for twice. The precipitates by vacuum drying at 60 °C gave a viscoelastic solid (1.41 g; yield 74%). ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.2–7.6 (3H, ArH), 3.21 (4H, −CH$_2$CH$_2$−), 0.16 (3H, Si−CH$_3$), 0.05 (2H, SiCH$_2$Si).

2.6. Synthesis of polystyrene with benzocyclobutene/silacyclobutene pendant groups (P2)

In a typical experiment, styrene (4.0 mL, 35 mmol), 4-VBCB (1.30 g, 10 mmol), 1-MVPSCB (0.94 g, 5 mmol), Cu(I)Cl (0.49 g, 5 mmol), Cu(II)Br$_2$ (0.10 g, 0.5 mmol), benzyl bromide (600 μL, 5 mmol), PMDETA (1.10 mL, 5 mmol) and toluene (5.0 mL) were sequentially added to a flask under nitrogen atmosphere. The flask was then placed in an oil bath at 100 °C for 24 h. The solution was diluted with THF and precipitated into 50 mL of methanol. The product (5.41 g, yield 92%) was obtained by repeated centrifugation in methanol followed by drying at 40 °C under vacuum for 24 h. ^{1}H NMR (600 MHz, CDCl$_3$) δ: 6.82–7.19 (2H, ArH), 6.13–6.82 (2H, ArH), 2.85–3.19 (4H, CH$_2$CH$_2$), 1.70–2.08 (2H, CH$_2$), 1.28–1.47 (6H, −Si−CH$_2$−CH$_2$−CH$_2$−), 0.55 (3H, Si−CH$_3$). The P2 has the structure of poly(St)$_{184}$(4-VBCB)$_{66}$(1-MVPSCB)$_{103}$ and M_w of 45000 g/mol.

2.7. Synthesis of polycarbosilane-graft polystyrene (P3, P4, P5)

Polycarbosilane-graft polystyrene were synthesized by reacting P2 with M3. In a typical experiment, M3 (0.19 g, 0.6 mmol), P2 (1.71 g, 0.038 mmol) and H_2PtCl_6 (10 μL) were dissolved in xylene (50 mL). The solution was allowed to react under nitrogen in reflux for 24 h. The solution was precipitated twice from tetrahydrofuran (THF) into petroleum ether to give solids. The solids were re-dissolved in THF, filtered