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ORIGINAL PAPER

Synthesis and characterization of polycarbonates containing terminal and chain interior siloxane

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Abstract Silicone polycarbonates having polydimethyl siloxane (PDMS) and heptamethyl trisiloxane (HMTS) were synthesized by the interfacial polymerization. Instead of common chain terminator *p*-tert-butyl phenol (PTBP), eugenol capped HMTS, and PDMS were used. PDMS was also attached into the chain interior of the polymer in different molar ratios. PDMS and HMTS were capped with eugenol through the hydrosilylation reaction using Karstedt's catalyst. Both monohydroxy and dihydroxy terminated eugenosiloxanes were synthesized in order to use as chain terminator and interior subunit of polymer, respectively. Structural characterization and the study of the properties, such as thermal behavior, thermooxidative stability, surface morphology, wettability of the synthesized polymers were investigated. Flexibility and wettability of the synthesized polymers increases with increasing of silicone content. Polymers showed satisfactory thermo oxidative stability and transparency as good as bisphenol-A-polycarbonate.

Keywords Silicone polycarbonate · Chain terminator · Hydrosilylation reaction · Thermal properties · Wettability

M. S. Islam Mollah and Young-Do Kwon are contributed equally to this study.

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Introduction

Because of their excellent physical and chemical properties, such as high transparency, high impact resistance, high heat distortion temperature, good thermal stability, and non flammability, polycarbonates (PC) are being used as major thermoplastic engineering polymer. However, to investigate and to improve their properties as well as to insure their versatile application in several industrial fields, numerous works have been done that include structural modifications, blend preparation with other polymers, coating on the surface, etc. In these purposes, various materials such as siloxanes, polysiloxanes, organosiloxanes, halogen, acrylate, acrylonitrile styrene, and phosphorus have been explored. Among them siloxanes and polysiloxanes are remarkable and have been widely used. As an engineering plastic material, scratch resistance is one of the important draw back of PC. To overcome this weak point, siliceous hard coating, and deposition of silica or organosilica on the polycarbonate substrates surface is a typical approach [1–5]. Recently, Kogoma and co-workers [6] deposited SiO_2 film on PC using both atmospheric glow plasma chemical deposition (APG-CVD) and spin coating as hard coating agents for abrasion resistance. Spin coating on surface over APG-CVD, as adhesive interlayer, could make a hard deposition film without cracking. Koda and co-workers [7] reported that vacuum ultraviolet irradiation on siliceous coating on PC substrate can harden the coating due to the mineralization of the coating in the direction to silica-like materials, and in parallel can improve the scratch resistance considerably. Polysiloxanes have also been used widely in polycarbonate blend as impact modifier. Besides other compounds such as methacrylate/butadiene/styrene copolymer (MBS), poly butylarylate (BA), acrylonitrile–butadiene–styrene terpolymer (ABS), etc., have also been explored [8–10]. As reported by Srinivas et al. [11] polycarbonate-polysiloxane copolymer has been used as an impact modifier in a flame retardant and scratch resistant thermoplastic polycarbonate composition. Recently, An et al. [12] used polysiloxane-polycarbonate copolymer to prepare polycarbonate composition with low temperature ductility. It is established that the halogen containing polycarbonates have been synthesized to improve the flame retardancy. However, due to the environment concern, many efforts have been made to develop halogen-free polycarbonate compositions that usually contain phosphorous-based compounds [1, 13–15]. Jiang and co-workers [16] synthesized and characterized novel halogen-free flame retardant compounds containing phosphorus, nitrogen, and silicon elements and studied their fire performance in PC/ABS alloy. Mahood et al. [17] reported eugenol-capped short-chain siloxane to prepare branched polysiloxane-polycarbonate block copolymers with good fire resistance and transparency.

Our group already reported about allyl functionalized polycarbonate precursors based on bisphenol-A (BPA) followed by the preparation of silicone containing polycarbonates that results the polymer with better thermal properties [18] and allyl functionalized siloxane grafted polycarbonates[19]. In this article, we synthesized and characterized a series of BPA-based silicone polycarbonates (Si-PC) having siloxane as chain interior subunit and terminal position. To vary the content of silicone in the polymer, siloxane chain interior subunit was used in different molar

ratios. It was expected that the resulting new polymers would exhibit better thermal properties with improved wettability and transparency.

Experimental

Materials

BPA, triethylamine (TEA), heptamethyl trisiloxane (HMTS), poly(dimethylsiloxane) (PDMS), eugenol, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) were purchased from Aldrich Chemical Company and used as received. Common reagents such as acetone, methylene chloride, sodium hydroxide, and chlorobenzene were used without further purification. TEA was used as a 15% (w/v) aqueous solution.

Measurements

The ^{1}H NMR spectra were recorded on a Bruker DRX (400 MHz) spectrometer by using $CDCl_3$ and TMS as solvent and internal reference, respectively. At a heating rate of 20 °C/min and under a gas flow rate of 50 mL/min, Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) were conducted by using Perkin-Elmer DSC7 and TGA S-1000, respectively. The molecular weight of polymers was determined relative to polystyrene standards by gel permeation chromatography (GPC) in THF as the eluent on a Perkin Elmer series 200 high-pressure-liquid chromatographer equipped with a set of four μ-styragel columns (500, 10^4, 10^5, and 100 Å) in series and a RI detector. Non contact mode Atomic force microscopy (AFM) (PSIA XE100, Korea) were employed to observe the topography of the synthesized polymer films by using P/N 910 M-NCHR tips. The contact angle was measured by a contact angle analyzer (Phoenix-300, Surface Electro Optics). The volume of the sessile water drop was controlled to about 0.2 μL by a micro-syringe. The average value of both sides of each drop was considered as a contact angle.

Synthesis of eugenosiloxane I (chain terminator)

Heptamethyl trisiloxane (HMTS) (13.55 g, 61 mmol), eugenol (10 g, 61 mmol), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) (0.05 g, 13.1 $\times$ 10^{-5} mol), and chlorobenzene (50 mL) were added to a 100-mL three-necked round-bottom flask fitted with condenser and nitrogen inlet, and refluxed for 40 h. The solution was cooled to room temperature and solvent was evaporated well under vacuum. The residue was dissolved in chloroform and silica gel was added to it. After stirring 1 h the mixture was filtered through the Celite and the filtrate was evaporated under vacuum to get transparent yellowish product. Yield: 95%. ^{1}H NMR ($CDCl_3$, ppm, δ): −0.148–0.023 (m, 21H, –Si–CH_3), 0.40–0.44 (t, 2H, Si–CH_2–CH_2–CH_2–), 1.49–1.56 (m, 2H, –CH_2–CH_2–CH_2–), 2.44–2.48 (t, 2H, –CH_2–CH_2–CH_2–), 3.78 (s, 3H, –OCH_3), 6.56–6.59 (d, 2H, Ar*H*).

Synthesis of eugenosiloxane II (chain terminator)

PDMS (19.4 g, 33.5 mmol), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) (0.05 g, 13.1×10^{-5} mol), and chlorobenzene (50 mL) were added to a 100-mL three-necked round-bottom flask fitted with condenser and nitrogen inlet, and heated with stirring. Eugenol (5 g, 30.5 mmol) in chlorobenzene was added slowly by using dropping funnel for 10 h. After completion of addition, reaction mixture was refluxed for further 36 h and cooled to room temperature. The product was dissolved in methylene chloride and extracted the pure eugenosiloxane II through strong basic solution. The methylene chloride layer was washed three times with acid solution. The product was worked out by following the same procedure as that of eugenosiloxane I. Yield: 83%. ^{1}H NMR ($CDCl_3$, ppm, δ): −0.153–0.146 (m, 48H, –Si–CH_3), 0.48–0.50 (t, 2H, Si–CH_2–CH_2–CH_2–), 1.50–1.58 (m, 2H, –CH_2–CH_2–CH_2–), 2.46–2.49 (t, 2H, –CH_2–CH_2–CH_2–), 3.79 (s, 3H, –OCH_3), 6.52–6.59 (m, 2H, Ar*H*), 6.73–6.75 (d, 1H, Ar*H*).

Synthesis of eugenosiloxane III (subunit)

PDMS (20 g, 34.5 mmol), eugenol (11.9 g 72.5 mmol), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) (0.05 g, 13.1×10^{-5} mol), and chlorobenzene (50 mL) were added to a 100-mL three-necked round-bottom flask fitted with condenser and nitrogen inlet, and refluxed for 40 h. The transparent brownish product was obtained by following the same procedure as that of eugenosiloxane I. Yield: 96%. ^{1}H NMR ($CDCl_3$, ppm, δ): −0.033 to −0.008 (m, 48H, –Si–CH_3), 0.48–0.52 (t, 4H, Si–CH_2–CH_2–CH_2–), 1.49–1.57 (m, 4H, –CH_2–CH_2–CH_2–), 2.45–2.49 (t, 4H, –CH_2–CH_2–CH_2–), 3.79 (s, 6H, –OCH_3), 6.58–6.59 (d, 4H, Ar*H*), 6.73–6.75 (d, 2H, Ar*H*).

Synthesis of polymers (I)/(II)

Bisphenol A (114 g, 0.5 mol) and 5.4 wt% aqueous NaOH solution (44.8 g, 1.12 mol) were added to a 3-L three-necked round-bottom flask, fitted with a nitrogen inlet and ice jacket. Phosgene (64.35 g, 0.65 mol) dissolved in methylene chloride (950 mL) was added slowly to the solution and stirred for 30 min. The methylene chloride and water layers were separated. The molecular weight of the oligomer in methylene chloride was about 1000. Methylene chloride layer (30 mL, bischloformate 0.0354 mol), eugenosiloxane chain terminator (I) or (II), (0.566 g or 1.1 g, 1.464 mmol, ∼4 mol% of bischloroformate) dissolved in NaOH (10 mL, 1 g) solution and aqueous solution of tetrabutyl ammonium chloride (75 wt%, 0.3 mL), which is used as a phase transfer catalyst, were placed in a 500-mL three-necked round-bottom flask. The reaction mixture was stirred for 2 h at room temperature by using a mechanical stirrer at a speed of 500 r.p.m. Aqueous layer (45 mL) and TEA (15 wt%, 30 μL) were added to the mixture and stirred it for more 3 h at a speed of 700 r.p.m. The methylene chloride layer was separated. TEA (15 wt%, 37 μL), Methylene chloride (15 mL), and NaOH solution (10 mL, 1.23 g) were added to the separated methylene chloride solution and the mixture was stirred

for 3 h more. The polymer solution was washed with distilled water, neutralized with HCl, and precipitated into a mixture of acetone and distilled water (50:50, v/v) to give a white granular polymer. $T_g = 137$ °C. $T_m = 217$ °C. ^{1}H NMR ($CDCl_3$, ppm, δ): −0.153–0.146 (m, 48H, –Si–CH_3), 0.49–0.54 (t, 2H, Si–CH_2–CH_2–CH_2–), 1.59 (s, 6H, –C(CH_3)$_2$–), 2.45–2.55 (t, 2H, –CH_2–CH_2–CH_2–), 3.78 (s, 3H, –OCH_3), 6.5–6.7 (m, 3H, Ar*H*), 6.9–7.1 (m, 8H, Ar*H*).

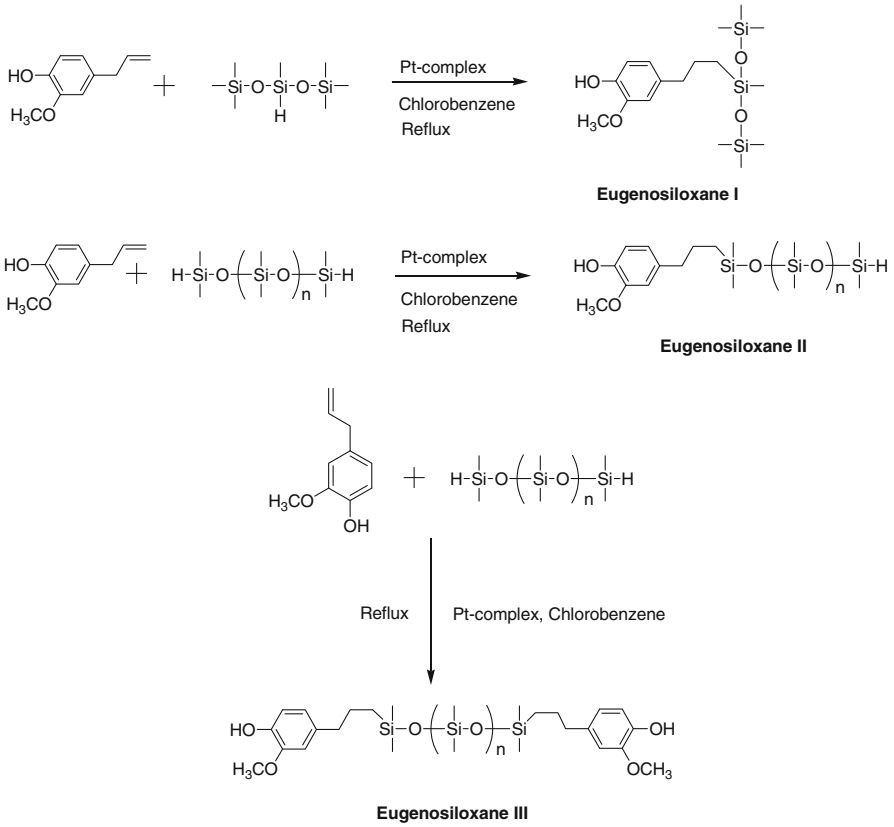
Synthesis of polymers III and IV

Polymers III and IV were synthesized according to the same procedure as that of polymers I and II. In these cases eugenosiloxane III as chain interior subunit, dissolved (sparingly) in NaOH solution, was added to the bischloroformate together with the eugenosiloxane II as chain terminator. $T_g = 82.55$ °C. $T_m = 211.93$ °C. ^{1}H NMR ($CDCl_3$, ppm, δ): −0.153–0.148 (m, 48H, –Si–CH_3), 0.49–0.54 (t, 2H, Si–CH_2–CH_2–CH_2–), 1.45–1.59 (m, 4H, –CH_2–CH_2–CH_2–), 2.45–2.55 (t, 2H, –CH_2–CH_2–CH_2–), 3.78 (s, 3H, –OCH_3), 6.59–6.61 (d, 6H, Ar*H*), 6.67–6.71 (d, 3H, Ar*H*), 6.9–7.1 (m, 8H, Ar*H*).

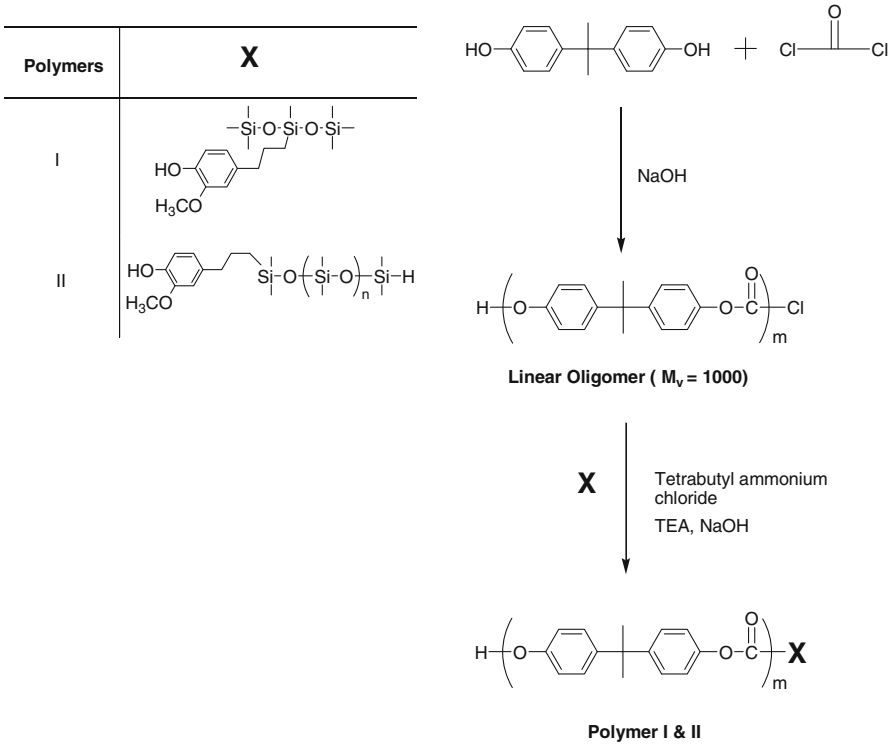
Results and discussion

Both monohydroxy and dihydroxy terminated eugenosiloxanes (eugenolsiloxane I, II, and III) were synthesized in order to use as chain terminator and interior subunit of polymer, respectively. Silicone polycarbonates were synthesized through the interfacial polymerization. For the convenient attachment of siloxane compounds to the polymer chain, hydride terminated heptamethyl trisiloxane (HMTS), and polydimethyl siloxane (PDMS) were capped with eugenol. Hydrosilylation reaction, which is an attractive route to form thermally and hydrolytically stable carbon silicone bond, provided convenient formation of new carbon silicon bond between allylic end carbon of eugenol and hydride terminated silicone (Scheme 1). This reaction was catalyzed by Pt-complex (Karstedt's catalyst) which typically proceeds to high conversions without the formation of byproducts [20]. However, the reaction of 1.1:1 mol ratio of PDMS and eugenol was resulted in a mixture of eugenolsiloxane II and III. The slow addition of eugenol into the pre-heated PDMS and catalyst was successfully achieved eugenolsiloxane II as a major product. Eugenolsiloxane II was purified by phase separation extraction method using methylene chloride and strong basic solution because dihydroxy terminated eugenolsiloxane III is more soluble in basic solution than Eugenolsiloxane II. The dihydroxy terminated eugenolsiloxane III was obtained by the reaction of 1:2.1 mol ratios of PDMS and eugenol. As depicted in Scheme 2, eugenosiloxane I and II (monohydroxy) acted as chain terminator whereas eugenosiloxane III (dihydroxy) attached to the polymer chain as interior subunit during the polymerization. Eugenosiloxane III was taken in two different molar ratios (about 5 and 10 mol% of bischloroformate) in order to vary the content of silicone in the polymer (Scheme 3). Tetrabutyl ammonium chloride (TBAC) was used as a phase transfer catalyst to facilitate the transfer of ionized eugenosiloxanes from the aqueous layer

to methylene chloride layer. The structures of the synthesized compounds were determined by ^{1}H NMR spectroscopy. Figure 1 shows the compiled ^{1}H NMR spectra of eugenosiloxane I, II, and III. Band ranging from δ −0.15 to 0.15 ppm corresponds to the methyl groups of HMTS or PDMS attached with silicone. The hydrogen's of carbon atom which is newly bonded with silicone shows peaks near δ 0.5 ppm. The band due to benzyl proton and aliphatic CH_2 group adjacent to the carbon which is bonded with silicone appeared near δ 2.5 and 1.5 ppm, respectively. The absence of band corresponding to allylic proton near δ 5.0 and 6.0 ppm and benzyl protonic peak near δ 3.2 ppm, which are the recognition of the eugenol structure as well as confirmed the complete attachment of eugenol with the siloxane compounds. Peak appeared near δ 5.3 ppm due to hydroxyl proton of eugenol. Aromatic and methoxy proton shows peaks ranging from δ 6.5 to 6.8 ppm and near δ 3.8 ppm, respectively, as expected. The compiled ^{1}H NMR spectra of synthesized Si-PC polymers were illustrated in Fig. 2. Hydroxyl protonic peak of eugenosiloxanes disappeared through the attachment with polymer chain. Peaks appeared near δ 1.6 and 7.0 due to the BPA unit. Other peaks correspond to the siloxane unit as these resemble to the spectra of monomers.

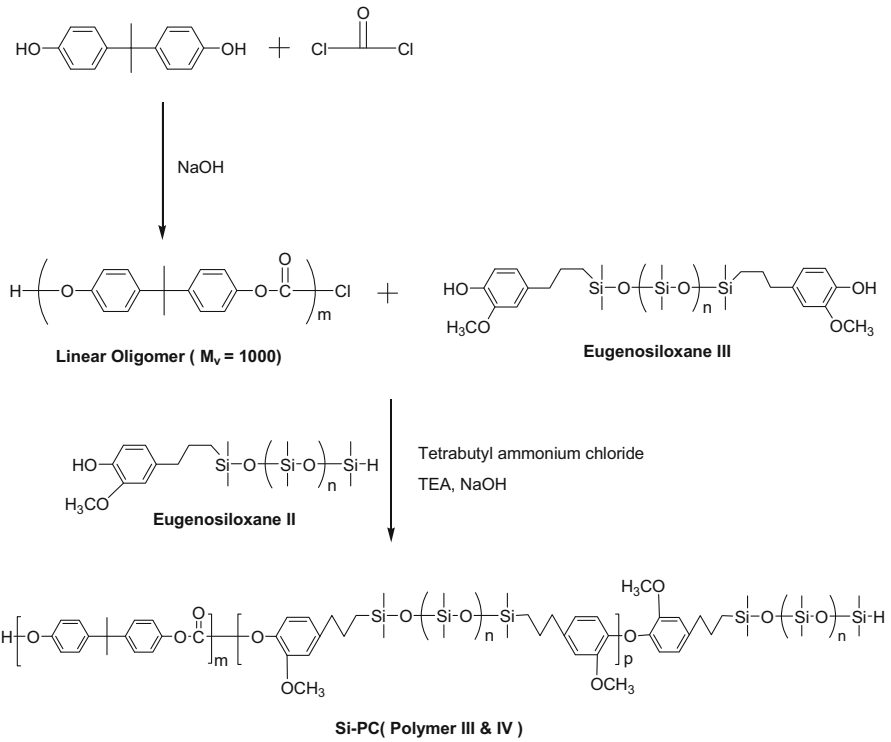


Scheme 1 Synthetic route for the preparation of eugenosiloxane monomers



Scheme 2 Synthetic route for the preparation of siloxane terminated polymers I and II

Thermal behavior of the polymers was investigated by differential scanning calorimetry (DSC). It is evident from Fig. 3 all the polymers have lower glass transition temperature (T_g) than that of commercial bisphenol-A-polycarbonate (BPA-PC) (150 °C). Polymer II exhibits lower T_g than that of polymer I. This means that the polysiloxane chain terminator could lower the T_g value in a higher magnitude compare to the trisiloxane chain terminator. But the lowest T_g value belongs to polymer III as it contains both the polysiloxane chain terminator and polysiloxane interior subunit. However, it is clear that the T_g values decreases with increasing of silicone content of the polymers. In fact, polymer IV didn't showed any T_g within our measurement range as its silicone content is too high because of the Si–O bond of siloxane, which can provide additional flexibility to the polymers. With the insertion of silicone monomer in polymer chain, the flexibility increased. The polymer film casted with polymer III is more flexible than polymer II or BPA-PC. The values of the T_g of the synthesized polymers were tabulated in Table 1. The thermooxidative stability of the polymers was studied by using thermogravimetric analysis (TGA). The TGA curves of the polymers shows in Fig. 4. Most of the polymer shows satisfactory thermal stability at high temperature in air atmosphere. The polymer that contains higher contents silicone shows a lower oxidative stability because the Si–O bond breaks at 300 °C. The molecular weight of the polymers was



Scheme 3 Synthetic route for the preparation of siloxane inside the chain and terminated polymers III and IV

determined by gel permeation chromatography (GPC). The synthesized polymers weight average molecular weight (M_w) and polydispersity (M_w/M_n) ranged from 45,000 to 55,000 and 2.2–2.0. As illustrated in Fig. 5, the GPC curve that corresponds to Si-PC (polymer III) showed the slightly expected left shift compared with linear polycarbonate. This result explained that the eugenosiloxane III monomer inside the polymer chain with eugenosiloxane II as chain terminator increased the polymer molecular weight.

Measurement of contact angle of sessile water drop onto the polymer film is a common and useful method, for understanding the wettability of the synthesized polymers. The water droplet on a highly hydrophobic surface shows a higher contact angle because of lower surface energy against the surface tension of the droplet and vise versa. It is believed that the incorporation of hydrophobic silicone into the polymer would lower the surface energy and eventually lower the wettability. As our anticipation, synthesized silicone polymers provided a higher contact angle than that of BPA-PC. Figure 6 illustrates the image of sessile water drop onto the polymer films. The curvature of the water surface made a higher contact angle in the

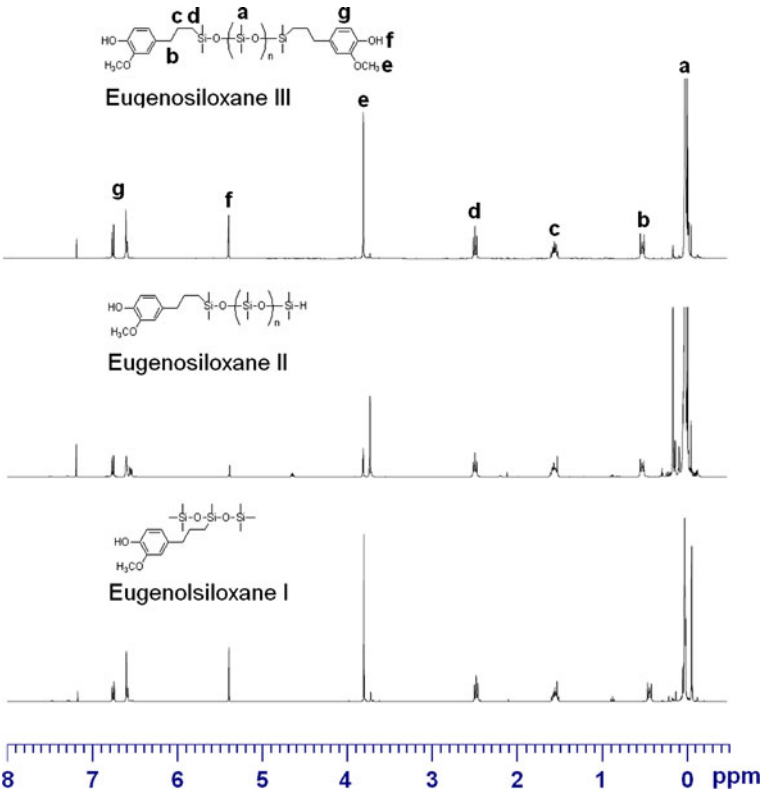


Fig. 1 ^{1}H NMR spectra of eugenosiloxanes

case of Si-PCs**.** As presented in Table 1, contact angle increases with increasing of silicone content of the polymers. The plot showed the linear increment of the contact angle as a function of the silicone content of the polymers (Fig. 7). This is because during the casting of films, the terminator siloxane came closer to each other through intermolecular forces of attraction, and lifted themselves up to the surface of film that provide additional hydrophobicity to it. Along with the length of terminal siloxanes or interior siloxane, the surface morphology of polymers were changed by phase separation of hydrophobic and hydrophilic domain size. The aforementioned reason is evident by AFM topography. The difference in surface morphologies between BPA- and Si-PC with different length of siloxane is illustrated in Fig. 8. As one can see, the surface of polymer I with the short length of siloxane showed much bumpy, but polymers II and III showed broad bumpy surface and linear BPA-PC showed smooth surface. Consequently, the surface morphology depends on the length of siloxane group and polymer matrix, which effect on phase separation of hydrophobic and hydrophilic domains. Beside the better wettability, polymers exhibit transparency as good as commercial BPA-PC which is unlike grafted silicone polycarbonate [19]. The physical and thermal properties of the polymers were compiled in Table 1.

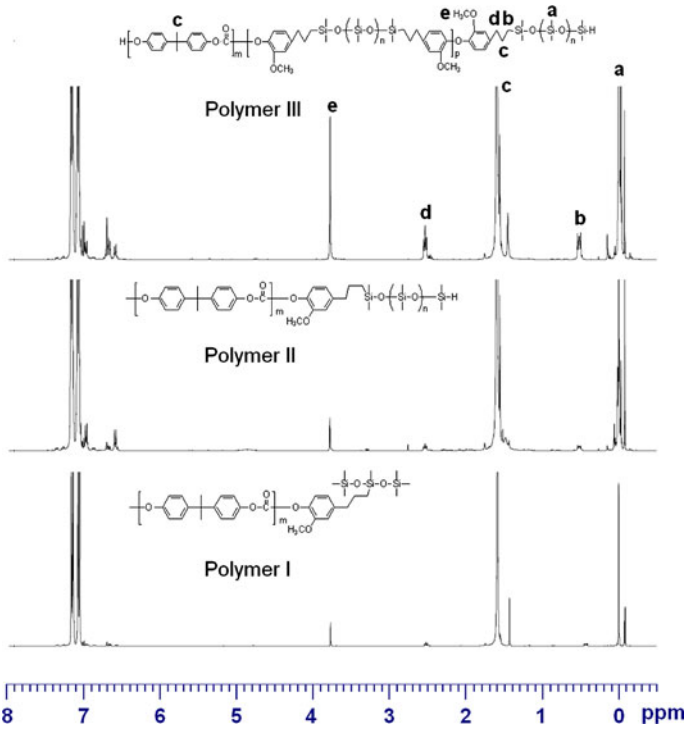


Fig. 2 ^{1}H NMR spectra of polymers I, II, and III

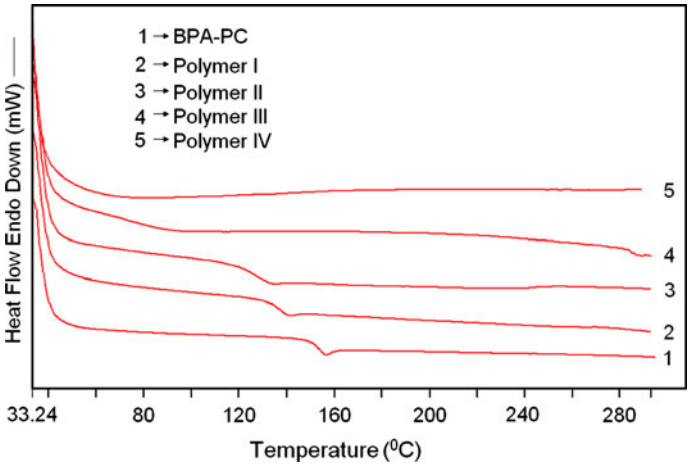


Fig. 3 DSC thermogram of the polymers

Table 1 Physical and thermal properties of polymers

Polymers	T_g/T_m (°C)	TGA (°C)	Contact angle θ (°)
Bisphenol A PC	151/223	380	83.12
Polymer I	137.34/217.10	379	83.21
Polymer II	129.07/218.96	304	86.77
Polymer III	82.55/211.93	323	87.2
Polymer IV	X	315	91.68

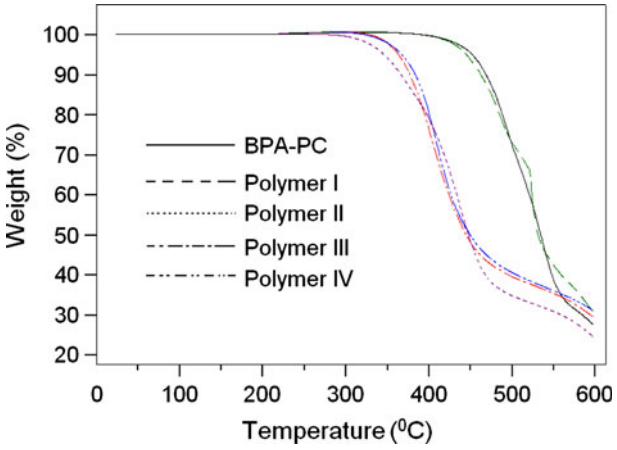


Fig. 4 TGA thermogram of the polymers

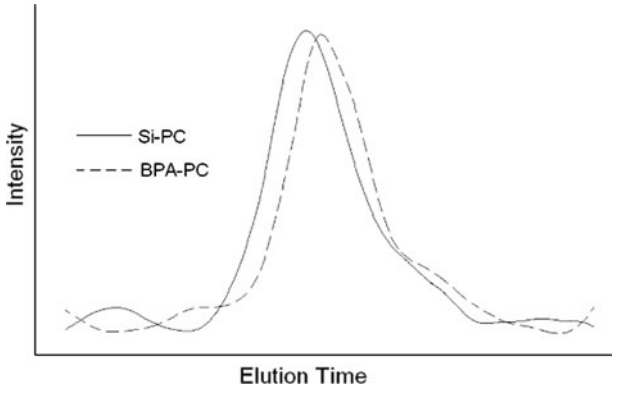


Fig. 5 GPC curves of BPA-PC and polymer III

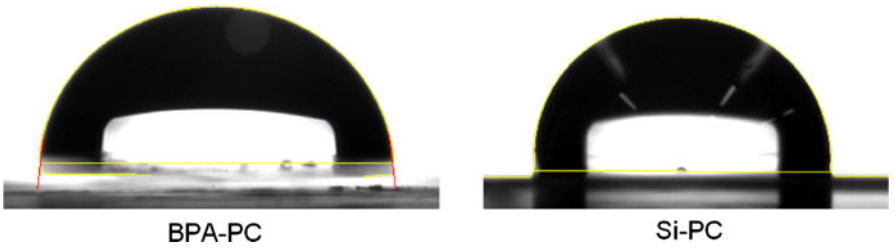


Fig. 6 Image of water droplets onto the polymer film of BPA- and Si-PC

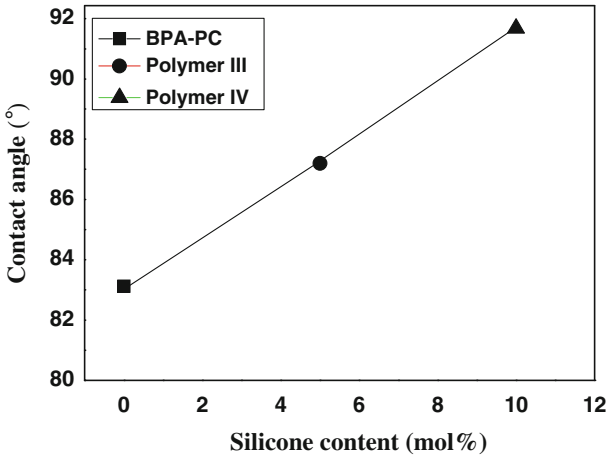


Fig. 7 Change of contact angle as a function of silicone content

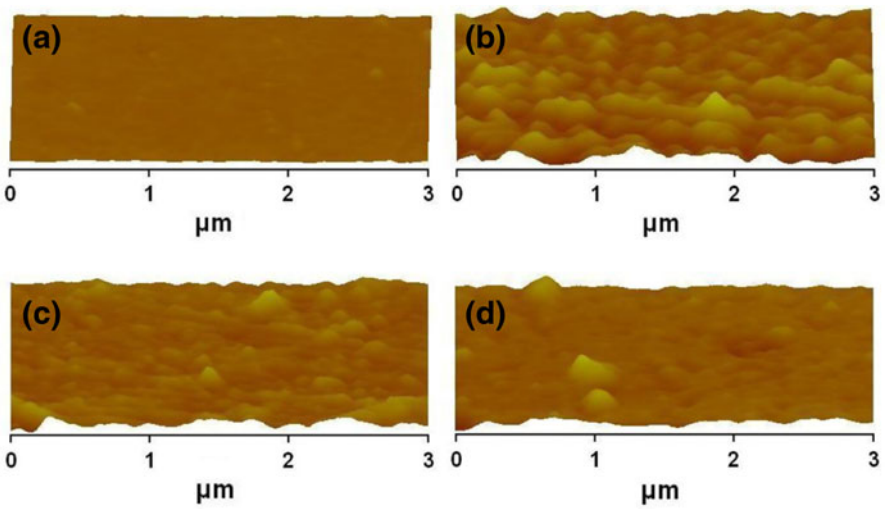


Fig. 8 AFM images of **a** BPA-PC, **b** polymer I, **c** polymer II, and **d** polymer III

Conclusions

Silicone polycarbonates containing siloxane compound in the chain interior and terminal position were synthesized and characterized. Siloxane subunit and chain terminators were synthesized through the hydrosilylation reaction using Karstedt's catalyst. Polymers were more flexible and wettable than that of commercial BPA-PC. Flexibility and wettability of the polymers increases with increasing of silicone content. Unlike the grafted silicone polycarbonates, these polymers showed excellent transparency. These compounds can be used for preparing particular objects that need additional flexibility and lower wettability with high thermooxidative stability and transparency for their convenient use.

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References

1. Jang BN, Jung IC, Yun JH, Choi JH (2007) Scratch-resistant flameproof thermoplastic resin composition. WO Patent 2007/119920 A1
2. Yung-Sen L, Ying-Huei L, Mao-Syuan W (2009) Enhanced scratch resistance of polycarbonate by low temperature plasma polymerized organosilica. Thin Solid Films 517:5224–5230. doi:10.1016/j.tsf.2009.03.181
3. Gabelnick AM, Lambert CA, Warakomski JM, Aerts LM (2006) Abrasion resistant coatings by plasma enhanced vapor deposition. WO Patent 2006/049794 A2
4. Hwang DK, Moon JH, Shul YG, Jung KT, Kim DH, Lee DWJ (2003) Scratch resistant and transparent UV-protective coating on polycarbonate. J Sol-Gel Sci Techn 26:783–787
5. Pickett JE, Sargent JR, Blaydes HA, Babbie N (2009) Effects of temperature on the weathering lifetime of coated polycarbonate. Polym Degrad Stabil 94:1085–1091. doi:10.1016/j.polymdegradstab.2009.04.001
6. Masuda S, Tanaka K, Kogoma M (2008) Deposition of SiO_2 thin films by atmospheric pressure glow plasma on polycarbonate. J Photopolym Sci Tech 21(2):263–266
7. Tsuzuki Y, Oikubo Y, Matsuura Y, Itatani K, Koda S (2008) Vacuum ultraviolet irradiation on siliceous coatings on polycarbonate substrates. J Sol Gel Sci Techn 47:131–139. doi:10.1007/s10971-008-1768-2
8. Gosens JC, Leonardus AH, Eugene HJ (1995) Polymer mixture comprising an aromatic polycarbonate, a styrene-containing copolymer and/or graft polymer, and a polysiloxane-polycarbonate block copolymer, and articles formed therefrom. US Patent 5,380,795
9. Hoover JF (2003) Polycarbonate-polysiloxane block copolymers. US Patent 6,657,018
10. Umeda T, Okamoto M (1996) Polycarbonate resin composition. US Patent 5,488,086
11. Srinivas S, Agarwal N, Lens JP (2008) Flame retardant and scratch resistant thermoplastic polycarbonate compositions. US Patent 20080015291 A1
12. An Y, Chen J, Jiao H, Lin Y, Tjahjadi M, Yang X (2009) Polycarbonate compositions and articles formed therefrom. US Patent 7,553,895
13. Lee BJ, Kim KT, Min SS (2007) Flame retardant polycarbonate resin composition having good impact, high heat resistance. US Patent 20070155857 A1
14. Ebeling T, Marugan MM, Qu Z, Siripurapu S (2006) Flame retardant thermoplastic polycarbonate compositions, use and method of manufacture thereof. European Patent EP 1 624 025 A1
15. Hong SH, Jung HJ, Ku JH (2006) Flame retardant polycarbonate resin composition. WO patent 2006/070982 A1
16. Zhong H, Wei P, Jiang P, Wu D, Wang G (2007) Synthesis and characteristics of a novel silicon-containing flame retardant and its application in poly[2,2-propane-(bisphenol) carbonate]/acrylonitrile butadiene styrene. J Polym Sci Part B Polym Phys 45:1542–1551. doi:10.1002/polb.21151

17. Mahood JA, Niles RR, Rajendra KS (2003) Transparent, fire-resistant polycarbonate composition. US Patent 2003/0027905 A1
18. Sang HK, Woo HG, Kim SH, Kim JS, Kang HG, Kim WG (1999) Synthesis and properties of allyl-terminated and silicone containing polycarbonates. Macromolecules 32(19):6363–6366. doi:10.1021/ma99011893
19. Islam Mollah MS (2010) Synthesis and characterization of silicone polycarbonates. M. S thesis. Konkuk University, Chungju
20. Lestel L, Cheradam H, Boileau S (1990) Crosslinking of polyether networks by hydrosilylation and related side reactions. Polymer 31:1154–1158. doi:10.1016/0032-3861(90)90266-2