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Synthesis and Characterization of Poly[(methylsilyleneethynylenephenyleneethynylene)s-co-decamethylpentasiloxane]

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Poly[(methylsilyleneethynylenephenyleneethynylene)s-co-decamethylpentasiloxane] was synthesized by polycondensation reaction of di-Grignard reagent of diethynylbenzene with 1,9-dichlorodecamethylpentasiloxane and dichloromethylsilane. The copolymer is a liquid and soluble in common organic solvent at room temperature. The copolymer was characterized by FTIR, ¹H-NMR, rheological analysis, and differential scanning calorimetry. The results show that the copolymer exhibits good processability and cures at about 170°C. The copolymer can be thermally cured to produce highly crosslinked copolymer. The thermal stability of the cured copolymer was measured by thermogravimetric analysis. The degradation temperature at 5% weight loss is 591°C and the residue yield at 1000°C is 86% in N₂. Black, hard, and glassy ceramic was produced when the cured copolymer was heated above 1450°C under argon. The ceramic has high thermooxidative stability.

Keywords: Diethynylbenzene, siloxane, methylsilylene, thermal stability, inorganic-organic hybrid polymers, high-performance polymer

1 Introduction

Silicon-containing polymers have been intensively studied because of the possibility of application in the fields of ceramics, optical materials, and conducting materials (1, 2). There is current interest in the synthesis and properties of silicon-containing polymers composed of silicon acetylene units in the polymer backbone (3–10). In these polymers, poly[(phenylsilyleneethynylene-1,3-phenyleneethynylene)] (named MSP) is synthesized by dehydrogenative coupling polymerization reactions between phenylsilane and *m*-diethynylbenzene. The cured MSP polymer possesses high decomposition temperature and residue yield at 1000°C. Many papers concerning with MSP polymer have been published (11–13). Researchers in our group have focused on the design and synthesis of linear arylacetylene polymers containing inorganic components (14, 15). Arylacetylene unit can provide the site for crosslinking and conversion to the thermoset without

the formation of volatile byproducts (16, 17). Our further research efforts are mainly concerned with the synthesis of liquid or solid polymers with low melting temperature, which could be converted into thermosets and/or ceramics with good mechanical, thermal, and oxidative properties. Siloxanes possess good thermal and oxidative stability and hydrophobicity (18). However, the arylacetylene polymer containing siloxane units demonstrates low thermal decomposition temperature (19). Si-H group can react with many chemical groups such as C=C, C≡C, C=O, OH, NH, and C≡N. Introduction of Si-H group into the arylacetylene polymers containing siloxane units would improve the properties of the resulting polymer.

In this paper, a new copolymer, poly[(methylsilyleneethynylenephenyleneethynylene)s-co-decamethylpentasiloxane], was synthesized and its structure and properties were investigated.

2 Experimental

2.1 Materials

All syntheses were performed under dry nitrogen. Ethyl bromide (EtBr), magnesium powder, tetrahydrofuran (THF), hexane, silica gel, phosphorus pentoxide (P₂O₅),

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carbon tetrachloride (CCl₄), palladium dichloride (PdCl₂) were purchased from Sinopharm Chemical Reagent Co. Ltd. Tetrahydrofuran (THF) was refluxed over sodium with benzophenone and freshly distilled in nitrogen before use. Carbon tetrachloride (CCl₄) was distilled over P₂O₅. Dichloromethylsilane (DCMS) was purchased from Zhejiang Wynca Chemical Group Co., Ltd and distilled before use. Ethyl bromide was distilled before use. Dimethylchlorosilane was purchased from Shanghai Sili Gongmao Co. Ltd. and used as received. Hexamethylcyclotrisiloxane (D₃) was purchased from Shanghai Hua Run Chemicals Co. Ltd. and used as received. *m*-Diethynylbenzene was supplied by Fine Chemical Institute of East China University of Science and Technology and used as received.

2.2 Characterization

¹H-NMR analyses was performed on a BRUKER AVANCE 500 (500 Mz) instrument, using tetramethylsilane (TMS) as an external standard in CDCl₃ solution. Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 550 spectrometer. Number average molecular weight (\overline{M}_n) and weight average molecular weight (\overline{M}_w) of copolymers were characterized with multi-detectors GPC equipped with a DAWN HELEOS static laser scattering detector and an Optilab Rex refractive index detector, which is produced by Wyatt Technology Corporation. GPC analysis was performed using THF as an eluent at a flow rate of 1 mL/min. The rheological analyses were conducted on a rotational rheometer (HAAKE RS600). Differential scanning calorimetric analyses (DSC) were performed on a NETZSCH 200 PC module. Thermogravimetric analyses (TGA) were performed on a TA Instruments SDT Q600 analyzer. All thermal analyses were conducted at a heating rate of 10°C/min.

2.3 Synthesis of Monomers

2.3.1. 1,1,3,3,5,5,7,7,9,9-Decamethylpentasiloxane (DMPS) (20)

To a four-neck 500 mL flask fitted with a stirring bar, reflux condenser, nitrogen inlet, and dropping funnel were added water (72.0 g, 4.00 mol), D₃ (88.0 g, 0.40 mmol), silica gel (10.0 g) and hexane (100 mL). After the reagents were mixed enough under stirring, dimethylchlorosilane (113.4 g, 1.20 mol) was transferred to a dropping funnel and added dropwise to the rapidly stirring mixture over 2 h at room temperature. After the resulting suspension solution was continually stirred for 4 h, the silica gel was filtered off and the byproducts with low-boiling temperature were removed on a rotary evaporator. The residue was extracted with 125 mL benzene. The extracted solution was washed with water, a solution of NaHCO₃, and again with water. The organic layer was separated and dried over sodium

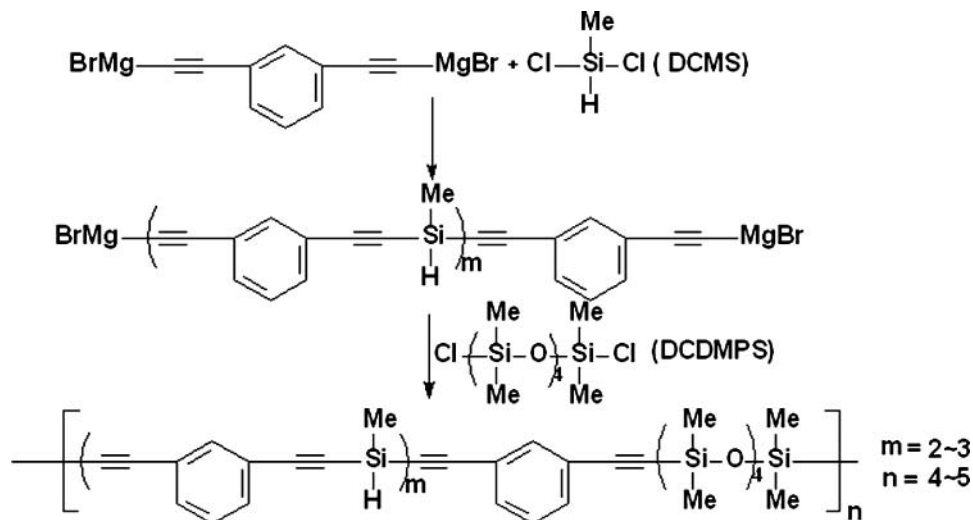
sulfate. The solvent benzene was evaporated on a rotary evaporator. The crude product was distilled and the fractional product at 89°C under the pressure of 15 mmHg was collected to give a pure product DMPS of 66.92 g as a colorless liquid. Yield: 47%. B.p.: 89°C at 15 mmHg. ¹H-NMR (CDCl₃, δ , ppm): 0.08 (d, 18H, O-Si(CH₃)₂-O), 0.19 (d, 12H, O-Si(CH₃)₂-O-Si(CH₃)₂-H), 4.71 (m, 2H, O-Si(CH₃)₂-H).

2.3.2. 1,9-Dichlorodecamethylpentasiloxane (DCDMPS) (21)

To a four-neck 250 mL flask fitted with a magnetic stirring bar, reflux condenser, nitrogen inlet, and dropping funnel were added PdCl₂ (0.08 g), and CCl₄ (100 mL). When the mixture in the flask was stirred, a solution of DMPS (26.8 g, 0.20 mol) in CCl₄ (50 mL) was added dropwise to the stirring mixture from a dropping funnel over 2 h at room temperature. The resulting suspension solution was continuously stirred for 72 h at room temperature. Thereafter, PdCl₂ was filtered off and the solvent was evaporated on a rotary evaporator. The crude product was distilled and the fractional product at 138°C under the pressure of 20 mmHg was collected to give the pure product DCDMPS of 32.48 g as a colorless liquid. Yield: 80%. B.p.: 138°C at 20 mmHg. ¹H-NMR (CDCl₃, δ , ppm): 0.15 (d, 18H, O-Si(CH₃)₂-O), 0.47 (s, 12H, O-Si(CH₃)₂-Cl).

2.4 Synthesis of Poly[(methylsilyleneethynylene-phenyleneethynylene)s-co-decamethylpentasiloxane] (PMED)

To a four-neck 250 mL flask fitted with a magnetic stirring bar, reflux condenser, nitrogen inlet, and dropping funnel were added magnesium powder (2.30 g, 96.0 mmol) and anhydrous THF (30 mL). A solution of ethyl bromide (23.98 g, 83.0 mmol) in anhydrous THF (30 mL) was transferred to the dropping funnel and added dropwise to the rapidly stirred mixture over 1 h at room temperature, and the mixture was reacted while being refluxed over 2 h to produce ethylmagnesium bromide. A solution of *m*-diethynylbenzene (5.04 g, 50.0 mmol) in anhydrous THF (30 mL) was then transferred to the dropping funnel and added dropwise to the rapidly stirred mixture over 1 h at room temperature, and the reaction was continued for an additional 1 h while being refluxed. The resulting white mixture was cooled in an ice bath. A solution of DCMS (3.89 g, 33.8 mmol) in THF (15 mL) was dropwise added to the above flask at room temperature over 30 min and the reaction further developed for another 2 h at the refluxing condition. The white di-Grignard reagents disappeared and the color of the solution changed to dark green. This mixture was cooled in an ice bath. A solution of DCDMPS (4.78 g, 11.3 mmol) in anhydrous THF (15 mL) was then added dropwise at room temperature over about 1 h, and the formed mixture was further reacted for 1 h while being refluxed. Thereafter, a solution of acetic acid (3.60 g,



Sch. 1. Synthesis of the copolymer PMED.

60.0 mmol) in toluene (50 mL) was added to the flask cooled with an ice bath, and then 2% aqueous solution of hydrochloric acid (50 mL) was added to the flask. The resulting oil phase was separated by using a separation funnel and washed with deionized water until neutral. The solvent was evaporated on a rotary evaporator to give the copolymer product as a yellow and high viscous liquid. The synthesis route is shown in Scheme 1.

2.5 Thermal Curing of the Copolymer PMED

The copolymer PMED was thermally cured according to the procedure: 150°C for 2 h, 170°C for 2 h, 210°C for 2 h, 250°C for 2 h, and 300°C for 2 h. Then, the cured product was allowed to cool slowly to room temperature and a shiny void-free cured copolymer C-PMED was obtained.

2.6 Thermal Pyrolysis of the Cured Copolymer (C-PMED)

The cured copolymer (C-PMED) was heated under argon according to the procedure: 400°C for 2 h, 600°C for 2 h, 800°C for 2 h, 1000°C for 2 h, 1200°C for 2 h, and 1450°C for 6 h, and then cooled to room temperature. A hard and black ceramic (CC-PMED) was obtained.

3 Results and Discussions

3.1 Synthesis of Poly[(methylsilyleneethynylene)phenyleneethynylene]-*co*-decamethylpentasiloxane] (PMED)

Poly[(methylsilyleneethynylene)phenyleneethynylene]-*co*-decamethylpentasiloxane] was prepared by the Grignard method (14). As shown in Scheme 1, di-Grignard reagent

of diethynylbenzene produced from diethynylbenzene and ethylmagnesium bromide ($\text{BrMg-C}\equiv\text{C-Ph-C}\equiv\text{C-MgBr}$) reacted with dichloromethylsilane (DCMS) to give an intermediate $\text{BrMg-[C}\equiv\text{C-Ph-C}\equiv\text{C-SiH(CH}_3)_2\text{-C}\equiv\text{C-Ph-C}\equiv\text{C-MgBr}$, and then the intermediate further condensed with 1,9-dichlorodecamethylpentasiloxane to produce a copolymer PMED in high yield (>85%). The number average molecular weight of the copolymer PMED was measured by GPC. The molecular number average weight for the copolymer PMED is 2022 and polydisperse index (PDI) 1.62.

Figure 1 shows FTIR spectrum of the copolymer PMED. The copolymer shows absorptions at 3290 cm^{-1} ($-\text{C}\equiv\text{CH}$), 3061 cm^{-1} (Ar-H), 2963 cm^{-1} (H-CH_2), 2155 cm^{-1} ($-\text{C}\equiv\text{C-}$, Si-H), 1590 cm^{-1} and 1473 cm^{-1} ($-\text{Ar-}$), $1100\text{--}1000\text{ cm}^{-1}$ (Si-O-Si), 1254 cm^{-1} and $882\text{--}789\text{ cm}^{-1}$ (Si- CH_3). These absorptions correspond with the structure of the copolymer as shown in the Scheme 1.

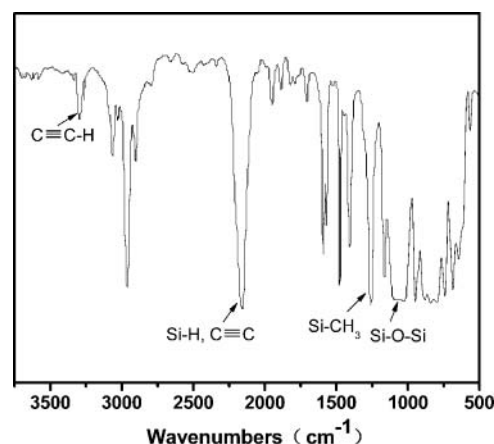


Fig. 1. FTIR spectrum for the copolymer PMED.

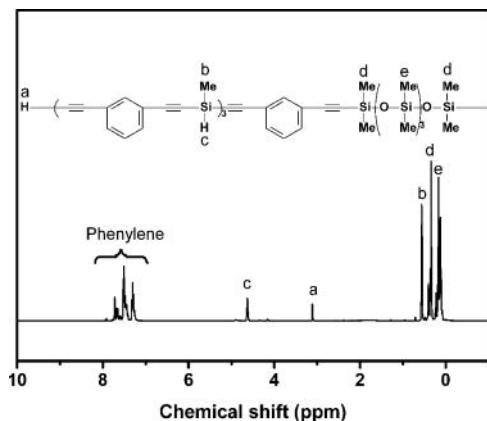


Fig. 2. ^1H -NMR spectrum for the copolymer PMED.

Figure 2 shows ^1H -NMR spectrum for the copolymer PMED. The dimethylsiloxy protons resonate in the 0.12–0.42 ppm region. The silicon methyl protons resonate at 0.56 ppm, while the protons bonded to silicon resonate at 4.6–4.7 ppm. In addition, the aromatic protons resonate in 7.2–7.8 ppm region and the protons of the terminal ethynyl groups resonate at 3.1 ppm. The molar ratio of protons in methylsilylene unit to decamethylpentasiloxane unit calculated based on the area of the peaks in ^1H -NMR spectrum is 0.32 which is consistent with the proposed structure. The characterization by ^1H -NMR confirms that the copolymer PMED has the expected chemical structures.

3.2 Solubility of the Copolymer PMED

Solubility of the copolymer PMED was investigated in various organic solvents. The copolymer PMED is soluble in common organic solvents such as benzene, toluene, chloroform, THF, acetone, butanone, and dimethylformamide (DMF) at room temperature. However, the copolymer PMED is insoluble in petroleum ether and methanol at room temperature. The good solubility of copolymer PMED is probably due to the effect of the siloxane units and Si-H groups in the polymer backbone.

3.3 Rheological Properties of the Copolymer PMED

Figure 3 shows the rheological curve of the copolymer PMED. As shown in Figure 3, the viscosity firstly decreases, then keeps constant, and finally increases dramatically with the increase in the temperature. Accordingly, the copolymer PMED firstly melts, and then keeps in the liquid state with constant viscosity, and finally reacts. The copolymer PMED melts at 50°C and the gelation reaction temperature of the copolymer PMED is 178°C. Obviously, the copolymer PMED possesses a broad processing window of 130°C. Conclusively, the copolymer PMED possesses good processability.

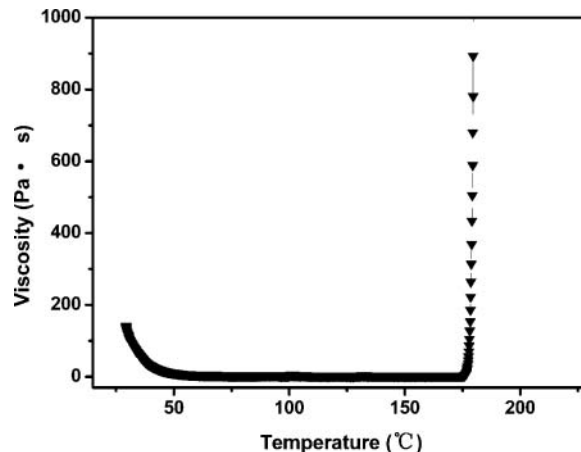


Fig. 3. Viscosity curve for the copolymer PMED.

3.4 Cure of the Copolymer PMED

Figure 4 shows the DSC curve for the copolymer PMED. The copolymer PMED shows a well-defined broad cure exotherm peak beginning at about 176°C with a maximum at 240°C. The amount of exotherm is 214.2 J/g. The exotherm is attributed to the crosslinking reactions: a hydrosilylation reaction between the Si-H and $\text{C}\equiv\text{C}$ groups and the polymerization of $\text{C}\equiv\text{C}$ groups. For the copolymer PMED, a shaped thermoset can be easily achieved through the thermal cure. The thermal cure of the copolymer is believed to proceed by the Diels-Alder reaction between Ph- $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{C}$ and the hydrosilylation reaction between Si-H and $\text{C}\equiv\text{C}$ to generate a network (13).

Figure 5 shows the FTIR spectrum of cured copolymer C-PMED. The peak at 3311 cm^{-1} shown in Figure 1, which is assigned to the C-H stretching of the terminal ethynyl group, disappears after cure shown in Figure 5. This demonstrates that all of the terminal ethynyl groups take part in the reaction. The intensity of the peak at 2156 cm^{-1} for $\text{-C}\equiv\text{C-}$ and Si-H obviously decreases, which implied Si-H and $\text{C}\equiv\text{C}$ groups participated in the curing reactions,

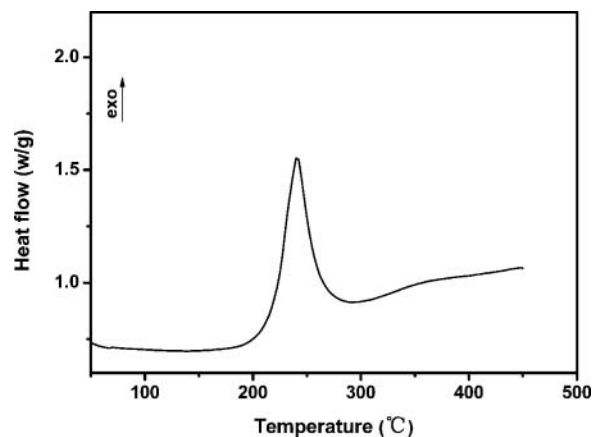


Fig. 4. DSC curve for the copolymer PMED.

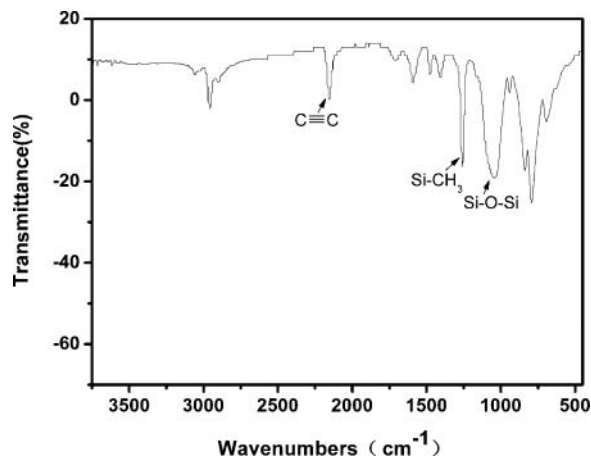


Fig. 5. FTIR spectrum for the cured copolymer C-PMED.

concerning the hydrosilylation reaction and Diels–Alder reaction. However, the peak still remains, suggesting that the reaction of $C\equiv C$ (internal ethynylene) groups does not reach the completion at this stage. The peak at 1260 cm^{-1} (Si–C stretching) along with a peak at 2970 cm^{-1} (C–H stretching of CH_3) and broad peak at $1000\text{--}1100\text{ cm}^{-1}$ (Si–O–Si stretching) indicate that the $\text{Si}(\text{CH}_3)_2\text{--O--Si}(\text{CH}_3)_2$ units are present after cure.

3.5 Thermal and Thermooxidative Stability of the Cured Copolymer C-PMED

Figure 6 shows the TGA curves for the cured copolymer C-PMED in both N_2 and air. The cured copolymer C-PMED exhibits a single-step process occurred for the decomposition in both N_2 and air. The cured copolymer C-PMED shows high thermal and thermooxidative stability, as shown in Figure 6. The decomposition temperature at 5% weight loss (T_{d5}) and the residue yield of the cured copolymer C-PMED in N_2 are 591°C and 86%, respectively. The decomposition temperature at 5% weight loss (T_{d5}) and the residue

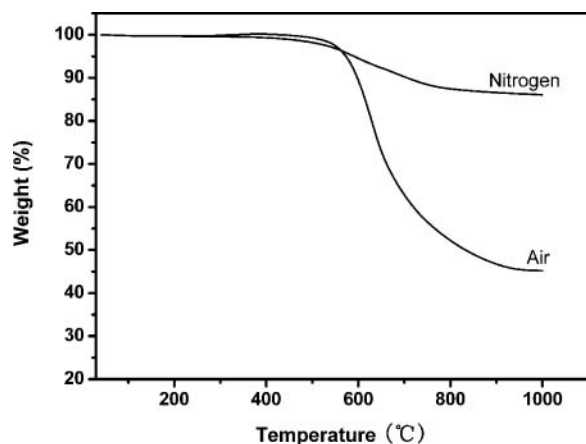


Fig. 6. TGA curve for the cured copolymer C-PMED.

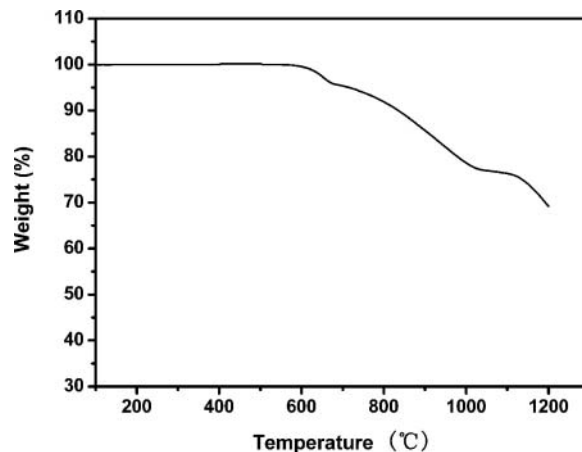


Fig. 7. TGA curve of the ceramic CC-PMED.

yield of the cured copolymer C-PMED in air are 572°C and 45%, respectively. The high thermal and thermo-oxidative stability of the cured copolymer C-PMED might be attributed to the presence of methylsilylene units and siloxane units in the polymer backbone and highly crosslinked network.

3.6 Thermooxidative Stability of the Ceramic CC-PMED

The ceramic CC-PMED obtained from the cured copolymer C-PMED pyrolyzed at 1450°C under argon. The ceramic yields of the cured copolymer C-PMED is 87.2%. These results illustrate that the copolymer is an excellent precursor for ceramics. The thermooxidative stability of the ceramic was investigated by TGA in air up to 1200°C . Figure 7 shows the TGA curve for the ceramic CC-PMED in air. As shown in Figure 7, the decomposition temperature at 5% weight loss for the ceramic CC-PMED is 743°C and the residue yield at 1000°C is 89.5% in air. The ceramic CC-PMED exhibits excellent thermooxidative stability. This is probably due to the introduction of methylsilylene units and siloxane units in the starting precursors.

4 Conclusions

Poly[(methylsilyleneethynylene)phenyleneethynylene]*s-co*-decamethylpentasiloxane] has been synthesized and characterized. The copolymer PMED is soluble in common organic solvents and exhibits good processability with a wide processing window (130°C) and a low curing temperature (176°C). The cured copolymer C-PMED has excellent thermal and thermooxidative stability with the degradation temperature of 591°C and 572°C at 5% weight loss in N_2 and air, respectively. A hard glassy ceramic was obtained when the cured copolymer C-PMED was heated up to 1450°C under argon. The degradation temperature of the ceramic CC-PMED at 5% weight loss is 743°C in air.

Acknowledgments

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