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Synthesis, characterization and thermal degradation of cross-linked polystyrene using the alkyne-functionalized esters as a cross-linker agent by click chemistry method

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Abstract

In this study, it has been demonstrated that cross-linked polystyrene (CPS) was successfully prepared by using click chemistry. For this purpose, firstly, poly (styrene-co-4 chloromethylstyrene) with 4-chloromethylstyrene was synthesized. Secondly, alkyne-functionalized esters (dipropargyl adipate, dipropargyl succinate) were obtained using propargyl alcohol, adipoyl chloride and succinyl chloride. Azide-functionalized polystyrene (PS-N₃) and dipropargyl adipate (or dipropargyl succinate) were reacted in N,N-dimethylformamide for 24 h at room temperature to give CPS. The synthesized polymer and compounds were characterized by nuclear magnetic resonance (¹H-NMR), gel permeation chromatography (GPC), fourier transform infrared spectroscopy (FT-IR) and thermogravimetric (TG/DTG) analysis. The surface properties were investigated by Scanning Electron Micrography (SEM).

Keywords: polystyrene, cross-linked polymers, click chemistry, thermal degradation.

1. Introduction

In last years, polystyrene (PS) has managed to become one of the world's most widely used polymers. PS is one of the three standard plastics (polyolefins, poly(vinyl chloride), and PS), and PS can be applied in many fields, such as the packaging of electrical equipment, apparatus, instruments, and foods, thermal insulation materials for buildings and cold storage, and disposable dinner service^[1]. However polystyrene do not offer the properties associated with thermoset polymers, and hence its applications are limited. Cross-linking of polystyrene is one approach to improve the properties and consequently to access the demanding regimes of high-tech applications. Crosslinked polystyrene (CPS) have excellent mechanical properties and good chemical stability. Their excellent performances provide wide applications as packing materials for liquid chromatography^[2-5], as ion-exchange resins^[6,7] and as imprinted adsorbents for the selective separation of hazardous organic compounds^[8,9]. Cross-linking of PS is readily achieved by the incorporation of a multifunctional monomer during the polymerization process^[10-15]. High-energy radiation or photochemical irradiation has been used, but in addition to the cross-linking both methods may also involve chain scission that can result in polymer degradation or the introduction of unwanted impurities. Alternative thermal methods for the formulation of thermosetting materials usually involve Diels-Alder and click chemistry reactions which may suffer from the reversibility^[16-17]. Yagci et al.^[15] synthesized polystyrene using click chemistry method. Other methods involves classical cross linker agent as DVB in literature. In our study, we introduce new strategy using both click chemistry method and new crosslinker agents (alkyne-functionalized esters).

2. Experimental

2.1 Materials

Styrene (S, 99%, Sigma-Aldrich Company, USA) and 4-chloromethylstyrene (CMS, ca. 60/40 meta/para isomer mixture, 97%, Sigma-Aldrich Company, USA) were distilled under reduced pressure before use. 2,2-Azobis(isobutyronitrile) (AIBN, 98%, Sigma-Aldrich Company, USA) was recrystallized from ethanol. Other solvents were purified by conventional procedures. Triethylamine (98%, Sigma-Aldrich Company, USA) and dichloromethane (99.9%, HPLC grade, Sigma-Aldrich Company, USA) were distilled from CaH₂. Noxyl- free radical (TEMPO, 99%, Sigma-Aldrich Company, USA) was used as received. Ethylenediaminetetraacetic acid (EDTA, 99%, Sigma-Aldrich Company, USA) N,N-dimethylformamide (DMF 99%, Sigma-Aldrich Company, USA). Propargyl alcohol (99%, Sigma-Aldrich Company, USA) were used without any purification. Pyridine (anhydrous, 98%, Sigma-Aldrich Company, USA). Adipoyl chloride (98%, Sigma-Aldrich Company, USA). Succinyl chloride (95%, Sigma-Aldrich Company, USA). 2,2'-bipyridine (reagent plus >99%, Sigma-Aldrich Company, USA). Copper(I) bromide (98%, Sigma-Aldrich Company, USA). Hydrochloric acid (ACS reagent, 37%, Sigma-Aldrich Company, USA).

2.2 Instrumentation

¹H-NMR (NMR, nuclear magnetic resonance) measurements were recorded in CDCl₃ (deuterium chloroform) with Si(CH₃)₄ as internal standard, using Varian AS-400 (400 MHz) instrument. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a PerkinElmer FTIR Spectrum

One-B spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL/min and a Waters 410 differential refractometer detector.

TG measurements of powders polymer samples were obtained on PerkinElmer Diamond TA/TGA from 25 to 1000 °C and heating rate of 10 °C/min under constant flow rate of 100 mL/min of nitrogen atmosphere. The sample weights for all the experiments were taken in the range of 8–10 mg. All SEM images were obtained by using a field emission scanning electron microscope Zeiss FE-SEM Supra 25 microscope under high vacuum at a voltage of 15.0 kV with a working distance of 6.0 mm.

2.3 Synthesis of poly(styrene-co-chloromethylstyrene)

Poly(styrene-co-4-chloromethylstyrene) (P(S-co-CMS)) was synthesized as described previously^[18].

2.4 Synthesis of polystyrene azide (PS-N₃)^[19]

A typical procedure for the preparation of PS-N₃ from 10 mol % CMS containing P(S-co-CMS) is as follows: P(S-co-CMS) (1.0 g, 1.04×10^{-4} mol) was dissolved in DMF, and NaN₃ (0.07 g, 1.01×10^{-3} mol) was added. The resulting solution was allowed to stir at 25 °C overnight and precipitated in excess methanol/water mixture (1/1 by volume). ¹H NMR (CDCl₃): δ ppm) 7.40–6.20 (b, 9H), 4.25 (s, 2H) FTIR T% (cm⁻¹): 3060, 2924, 2096, 1681, 1601, 1492, 1453, 757, 698. Mn: 3500 g/mol PDI: 1.50.

2.5 Synthesis of dipropargyl adipate (DPA, diprop-2-ynyl adipate) and dipropargyl succinate (DPS, diprop-2-ynyl succinate)

Propargyl alcohol (2.01 g, 0.036 mol), pyridine (2.69 g, 0.034 mol), and dry dichloromethane (20 mL) were charged to a 50 mL round-bottom flask. The resulting solution was maintained at 0 °C by means of a salt-ice bath. A solution of adipoyl chloride (2.63 g, 0.017 mol) or succinyl chloride (3.11 g, 0.017 mol) in 5 mL of dry dichloroethane was added dropwise over 30 min. The solution was stirred overnight at room temperature and then transferred to a 250 mL separatory funnel with the aid of a small amount of dichloromethane. The dichloromethane solution was washed with water (2×25 mL), 5% HCl (20 mL), and saturated sodium bicarbonate solution (25 mL). The dichloromethane solution was dried over MgSO₄ and the mixture was filtered. Organic phase was removed by evaporator. The products were dried under vacuum overnight. DPA: yield of 70%.

FTIR T% (cm⁻¹): 3294 (HC≡CH), 2920 (-CH₂-), 2126 (≡C-H), 1736 (-C=O), 1259 (-C-O-) ¹H-NMR (CDCl₃, 400 MHz, 25 °C, TMS): δ=1.76 (m, 4H, CH₂), 2.45 (m, 4H, CH₂-CO), 2.55 (t, 2H, ≡C-H), 4.72 (d, 4H, O-CH₂) ppm. DPS: yield of 65%. FTIR T% (cm⁻¹): 3289 (HC≡CH), 2920 (-CH₂-), 2128 (≡C-H), 1724 (-C=O), 1242 (-C-O-) ¹H-NMR (CDCl₃, 400 MHz, 25 °C, TMS): δ = 2.50 (m, 4H, CH₂-CO), 4.40(d, 4H, O-CH₂), 2.20 (t, 2H, ≡C-H).

2.6 Preparation of the crosslinked polystyrene by using DPA(C-PSA) and DPS(C-PSS)

In a flask, PS-N₃, DPA (or DPS), copper (I) bromide, 2, 2'-bipyridine and dry DMF were added. The flask was capped with a septum and purged with dry nitrogen for 10 min. The mixture was stirred overnight at room temperature. After removing the catalyst by EDTA, functionalized polymer was precipitated in methanol (200 mL), filtered, and dried under vacuum overnight with a yield of 70% (mol feed ratios are seen Table 1).

3. Result and Discussion

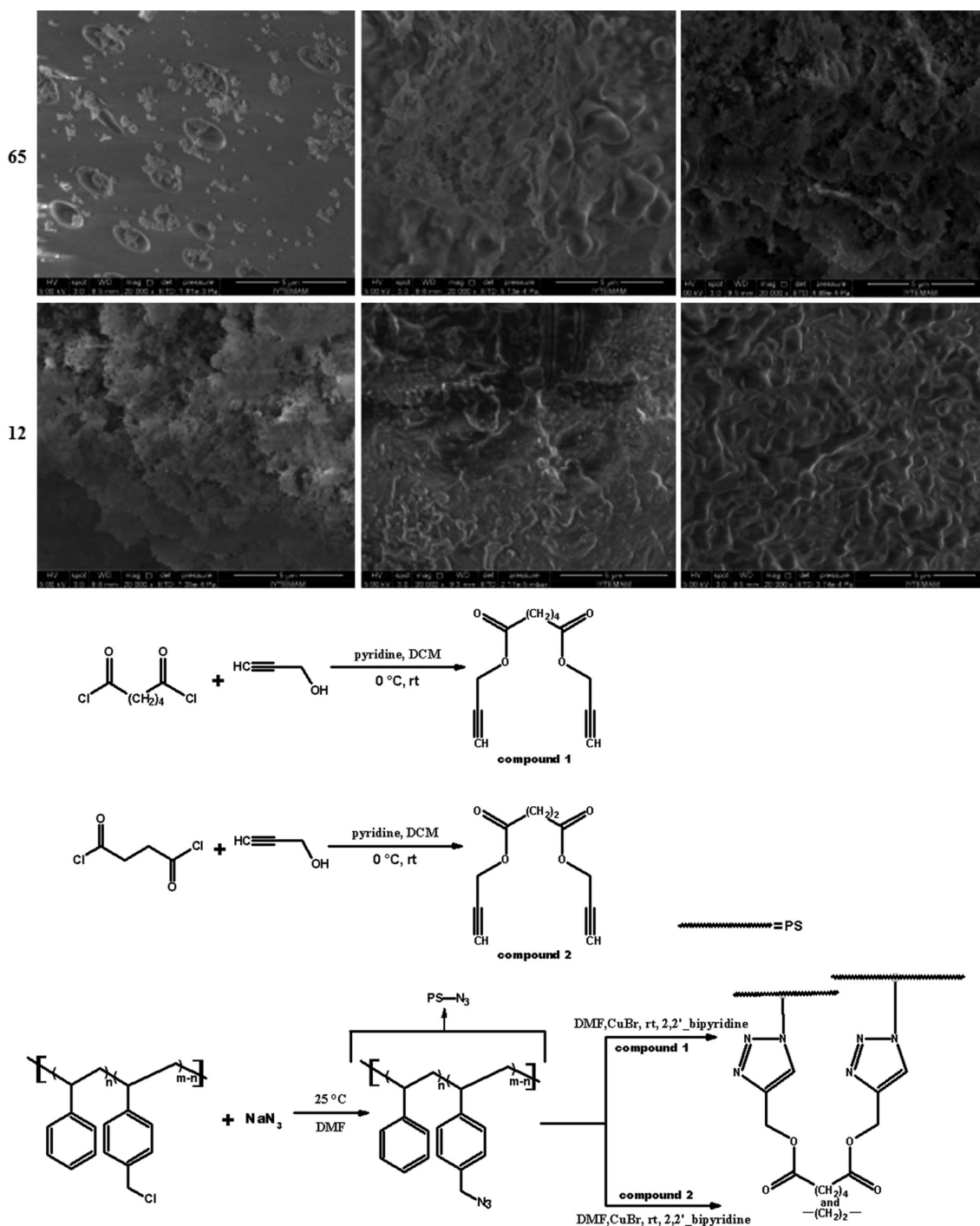
In our study, we first synthesized (P(S-co-CMS)) and P-N₃. Following experiment was carried out for alkyne-functionalized esters (DPA and DPS). DPA and DPS were used to obtain cross-linked polystyrene. CPS was synthesized via click chemistry (Scheme 1). Chemical structure of both esters and polymers were identified by several techniques such as FT-IR, NMR, GPC, TG, DTG and SEM.

The FT-IR spectra of DPA;PS-N₃;C-PSA_{65%};C-PSA_{12%} and DPS;PS-N₃;C-PSS_{65%};C-PSS_{12%} are shown in Figure 1 and Figure 2, respectively. According to this FT-IR spectra, appearance of the -N₃ stretching is clear at 2096 cm⁻¹ and it is notable that spectra of ADP and DPS show -HC≡CH-; ≡C-H- peaks at around 3290;2120 cm⁻¹. After cross-linked reaction between DPA(or DPS) and PS-N₃, disappearance of -N₃ and alkyne peaks can be seen. These FT-IR data show successful of PS-N₃, CPS, DPA and DPS synthesis. On the other hand, they are also supported by ¹H-NMR. From the ¹H NMR spectra of synthesized DPA and DPS, it is observed that -C≡H protons signals at 2.40 and 2.20 ppm, respectively. O-CH₂ protons are observed at 4.72(DPA) and 4.40(DPS) ppm. -CH₂-CO protons can be seen at 2.45 ppm and 2.50 ppm.

Thermal behaviour and thermal stability of the synthesized CPS is investigated by TG measurement. TG curves and the corresponding derivative curves (DTG) for cross-linked polystyrene are shown in Figure 3 and Figure 4, respectively. The derivative of the thermogram with respect to temperature,

Table 1. Mol feed ratio of synthesized cross-linked polymers.

Compound (C)	65% Azide Containing PS				
	CuBr	bipyridine	C	PS-N ₃	DMF
DPA	6.6×10 ⁻⁴ mol 0.094 g	1.3×10 ⁻³ mol 0.2 g	4.12×10 ⁻⁴ mol 0.092g	3.3×10 ⁻⁴ mol 0.1 g	5 ml
DPS	3.3×10 ⁻⁴ mol 0.0473g	6.6×10 ⁻⁴ mol 0.10g	2.10×10 ⁻⁴ mol 0.041g	1.68×10 ⁻⁴ mol 0.05g	5ml
Compound (C)	12% Azide Containing PS				
	CuBr	bipyridine	C	PS-N ₃	DMF
DPA	0.3×10 ⁻⁴ mol 0.042 g	0.6×10 ⁻⁴ mol 0.093g	1.87×10 ⁻⁴ mol 0.041g	1.5×10 ⁻⁴ mol 0.05g	5 ml
DPS	0.3×10 ⁻⁴ mol 0.042 g	0.6×10 ⁻⁴ mol 0.093g	1.87×10 ⁻⁴ mol 0.036g	1.5×10 ⁻⁴ mol 0.05g	5ml



Scheme 1. General procedure for the synthesis of alkyne functionalized ester containing CPS via click chemistry.

also known as a differential thermogram or DTG, indeed shows the maximum rate of polymer decomposition (T_{max}). TG thermogram under N₂ atmosphere revealed that C-PSA_{65%} and C-PSS_{65%} degradation takes place in three stages, C-PSA_{12%} and C-PSS_{12%} degradation takes place in two stages.

The first stage for the C-PSA_{65%} being at a temperature around 312 °C that corresponds to a very small mass loss

of about 10%. The second occurs at about 378 °C that corresponds to mass loss of about 25% and the last stage occurs at about 600 °C that corresponds to mass loss of about 50%. C-PSA_{12%} has two main decomposition stages. First one appears to begin around 291 °C and stop around 414 °C. The second one appears to begin around 390 °C and stop around 526 °C. The remaining mass without degradation of C-PSA_{65%} is higher than C-PSA_{12%}. When compared to

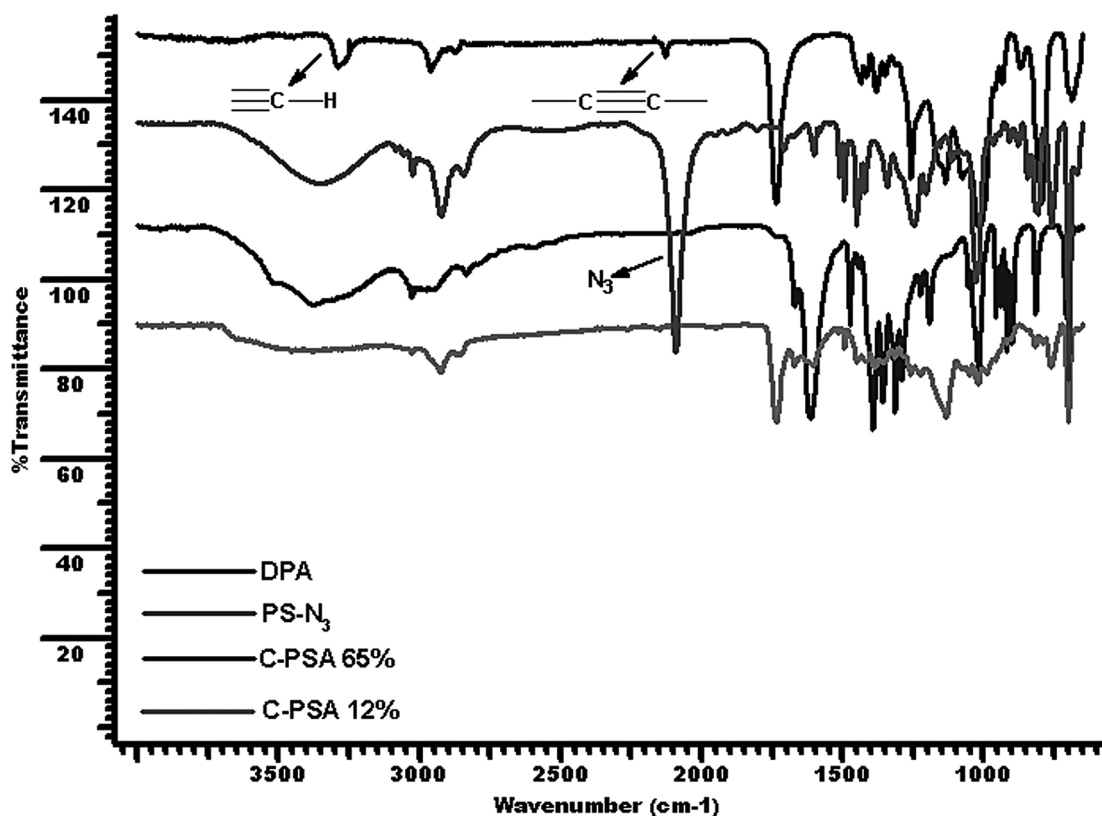


Figure 1. Comparison of FT-IR spectra of DPA;PS-N₃;C-PSA_{65%};C-PSA_{12%}.

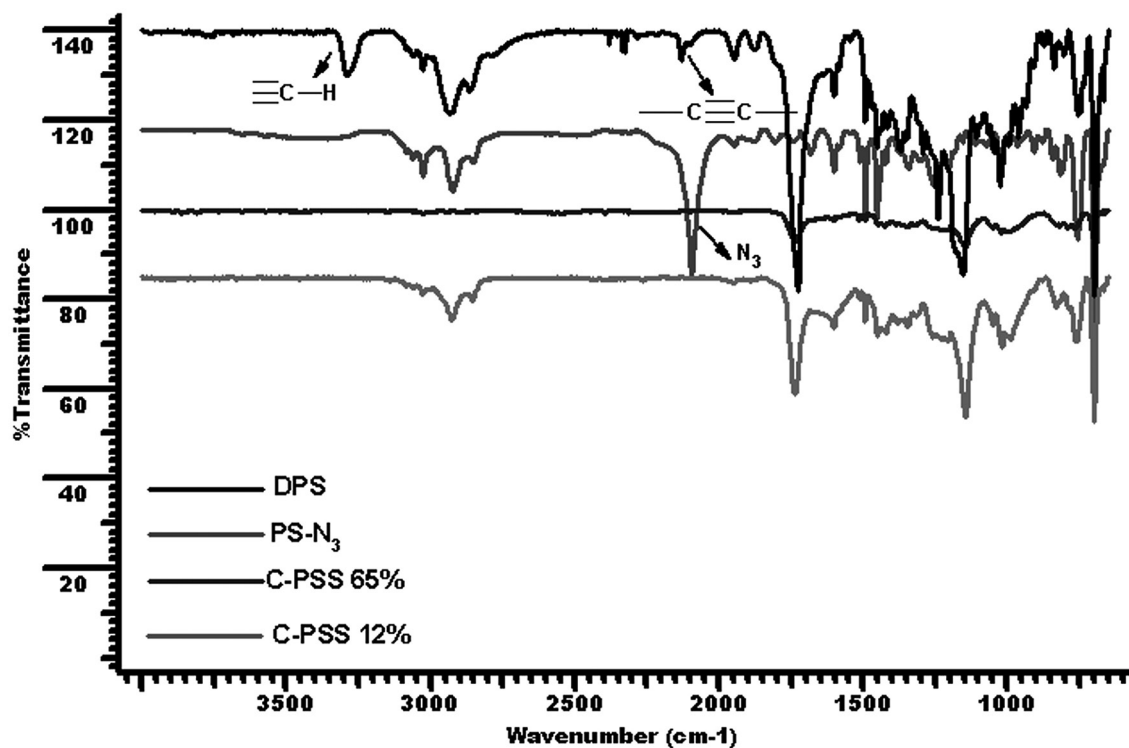


Figure 2. Comparison of FT-IR spectra of DPS;PS-N₃;C-PSS_{65%};C-PSS_{12%}.

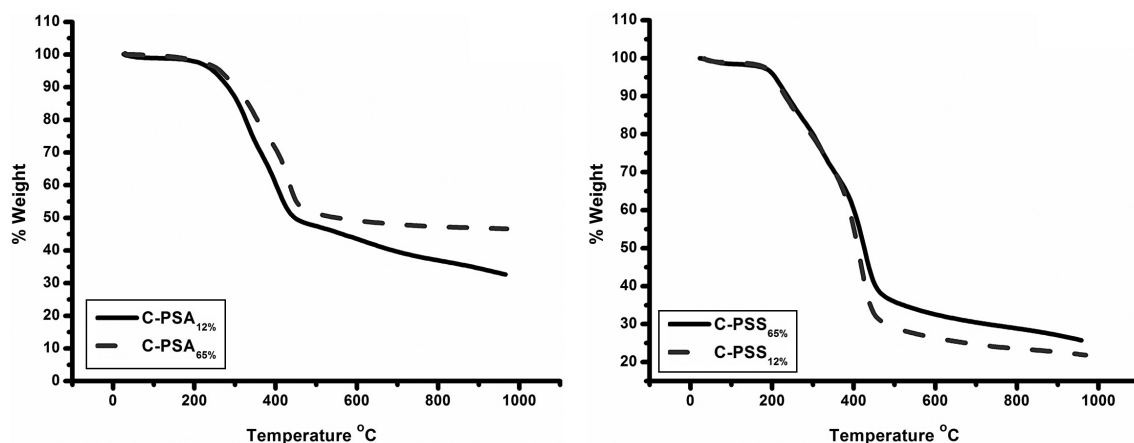


Figure 3. Comparison of TG curves of PSS_{65%}-C-PSS_{12%} and C-PSA_{65%}-C-PSA_{12%}.

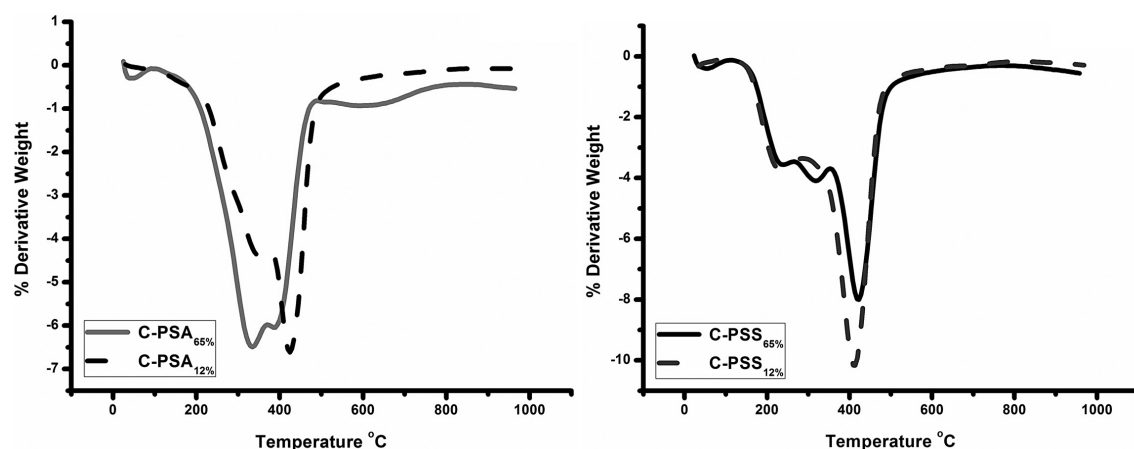


Figure 4. Comparison of DTG curves of C-PSA_{65%}-C-PSA_{12%} and PSS_{65%}-C-PSS_{12%}.

C-PSS_{65%} and C-PSS_{12%}, it is observed that C-PSS_{65%} more stable than C-PSS_{12%}.

The first, second and third degradation stages of C-PSS_{65%} begin 225, 296, 396 °C and the mass loss is about 10%, 20% and 75%, respectively. C-PSS_{12%} curves show two degradation stages which temperatures are 220 °C and 412 °C. When thermal degradation curves of polystyrene compared with crosslinked polystyrene, the char yield of the thermally cured polystyrene was about 40% and much higher than PS (0.0%) in literature^[15,20-22]. We also observed that thermal stability of CPS increases with the chain length of alkyne functionalized esters used (All Tmax values are shown in Table 2).

Table 3 displays the SEM micrographs obtained before and after cross-linked PS-N₃/DPA/DPS. The SEM microphotographs of PS-N₃ show that, most of the microspheres are irregularly spherical, and the interface is clear and smooth. The average particle size is between 1500µm-680 nm in diameter. The SEM images of various crosslinked PS, it could be visualized that no inert layer was formed on the surfaces of the C-PSS and C-PSA after cross-linked between PS-N₃ and alkyne functionalized esters. The images also indicate an increase in compact

Table 2. Tmax values of the synthesized cross-linked polystyrene.

CPS	C-PSS		C-PSA	
N ₃ %	12	65	12	65
Tmax(°C)	225	235	351	335
	412	320	423	387
	-	421	-	629

Table 3. SEM micrographs of PS-N₃, C-PSA_{65%}-C-PSA_{12%} and C-PSS_{65%}-C-PSS_{12%}.

Azid%	Sem micrographs of PS-N ₃	Sem micrographs of CPS after crosslinked	
		C-PSA	C-PSS

packing with increasing DPA or DPS content, suggesting the formation of a rigid interpenetrating network formation and increased crosslinking.

4. Conclusions

In conclusion, we introduce an effective strategy to synthesize a novel cross-linked polystyrene(C-PS) by using click chemistry. The Cross-linking reaction was

carried out under the condition of low temperature and we used the synthesized alkyne-functionalized esters as a cross-linker. According to data obtained from TG and DTG curves, chain length of alkyne functionalized esters plays important role for thermal stability and in char yield. PS cured in this way exhibited much more thermal stability than those of structurally similar cross-linked polymers. Surface morphologies of CPS changed when used cross-linker (DPA or DPS) of different chain lengths.

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