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Synthesis and Characterization of Polystyrene Possessing Triptycene Units in the Main Chain by Combination of ATRP and Click Chemistry Processes

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Polystyrene with triptcyene units were synthesized by combination of Atom Transfer Radical Polymerization (ATRP) and "Click" chemistry processes and characterized. Well-defined precursor polystyrene with predetermined molecular weight and narrow polydispersity was prepared by ATRP in the presence of Cu(I)/pentamethyldiethylenetriamine (PMDETA) catalyst system and terminal bromine groups of the obtained polymer were converted to azide group by using NaN_3. The click reaction between diazido compounds, namely diazido polystyrene (N_3-PSt-N_3) and diazidodecane (DAD) and dialkyne compounds, dipropargyloxytriptycene (DPT) and dipropargyloxydecane (DPD) resulted in the formation polystyrene with triptycene units in the main chain. Dialkyne compound without triptycene unit such as dipropargyloxybenzene (DPB) was used under the same click conditions for comparison. Characterization of the intermediates and the resulting polymers was performed by means of FT-IR and ^{1}H-NMR spectral analysis, and GPC, DSC and TGA studies. The effect of the triptycene moiety on the thermal properties was evaluated.

Keywords: ATRP, click chemistry, polystyrene, triptycene

1 Introduction

A large family of compounds wherein a number of arene units are joined together to form the bridges of [2.2.2] bicyclic ring system is called as iptycenes (1). The simplest member of the family, triptycene, has a rigid "paddlewheel" structure composed of three benzene rings that exhibit internal molecular free volume (IMFV) (2, 3). In the past decades, there is considerable interest in triptycene containing macromolecules as potential candidates for functional materials. Distinctly incorporation of triptycene units into polymer backbone may enhance lateral interactions via the minimization of internal molecular free volume or, specifically, the "threading" of polymer chains through triptycene cavities. Swager and coworkers (3) have extensively studied the high-performance polyester and conjugated polymer exhibited high stability and amplified fluorescent character (4). In liquid crystal applications by means of minimization IMFV, more proper and compact alignment of crystals occurs, because of a decrease in aspect ratio (length/width) (5–7). Iptycenes are also utilized to produce low dielectric constant polymeric materials having improved thermal stability and high T_g (8, 9). We have recently reported (10) a novel route to incorporate triptycene units into UV cured networks (Sch. 1).

For this purpose, a diacrylate cross-linker with triptycene units was synthesized and characterized. Moreover, the effect of triptycene moiety on the photopolymerization kinetics of various meth(acrylate) systems was evaluated. Notably, in the photopolymerization of these monomers, faster auto-acceleration and higher maximum rate of polymerizations were attained with the triptycene type cross-linker. The Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions between an azide and an alkyne, known as "click reactions" (11, 12) have gained a great deal of attention due to their high specificity, relatively mild reaction condition and nearly quantitative yields in the presence of many functional groups. This coupling process has been widely used for the modification of polymeric materials (13–19). In our laboratory, copper-catalyzed Huisgen 1,3-dipolar azide/alkyne, as well as Diels-Alder cycloaddition click reactions have been successfully used for functionalization of polymers (20–22), microsphere (23), clays (24)

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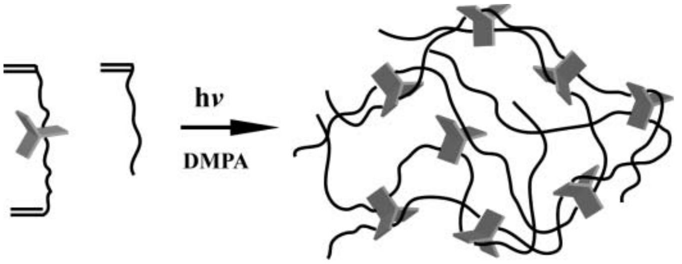


Sch. 1. Schematic representation of photo-induced cross-linking of vinyl monomers using triptycene containing diacrylate cross-linker.

and silsesquioxanes (25) with thermal-(26-28), photo-(20), and electro active (25) groups. The azide-alkyne click reaction has also been used to modify surfaces of various solid supports including silica spheres (29, 30), carbon nanotubes (31) even electrode (32) and glass surfaces (33–38). The 1,3-dipolar azide-nitrile cycloaddition has been used in the synthesis of well-defined polymeric tetrazoles (39). Furthermore, step-growth click coupling of telechelic polymers was performed by using α-alkyne-ω-azido-terminated polystyrene (40).

No doubt that the development of the controlled/living polymerization methods facilitated the synthesis of a wide range of complex macromolecules with well defined structures. Among various controlled radical polymerization methods developed in the last decade, ATRP (41-44) seemed to be the most extensively used method because of its easy manipulation, ability to control molecular weight and structure, and applicability to a wide range of monomers. Polymers prepared by ATRP are particularly suitable for subsequent end-group modification via Cu(I)-catalyzed azide-alkyne coupling because the halogen terminal groups that result from the polymerization can be easily converted to azide groups.

In this work, we report synthesis of polystyrene possessing triptycene unit in the main chain by the combination of ATRP and click chemistry process. Bromine terminal groups of polystyrene obtained by ATRP converted to azide functionality by simple nucleophilic substitution by using NaN_3. Bisalkyne functional triptycene compound was independently synthesized for the subsequent click reaction. Bisazide and bisalkyne functional compounds with long alkyl chain were also prepared and used as comonomers.

2 Experimental

2.1 Materials

Styrene (S, 99%, Aldrich) was distilled under reduced pressure before use. N, N, N', N'', N''-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was distilled before use. Anthracene (≥96%, Fluka) was purified via recrystallization from xylene. Tetrahydrofuran (THF, 99%, Fluka) was dried by distilling over benzophenone-Na before using. *N*, *N*-Dimethylformamide (DMF, ≥99%, Aldrich), sodium azide (NaN_3, ≥99%, Merck), CuBr (98%, Acros), sodium hydride (NaH, 98%, Fluka), acetone (99%, Fluka), propargyl bromide (80% volume in toluene, Fluka), potassium carbonate (K_2CO_3, ≥99%, Merck), hydroquinone (≥98%, Fluka), hydrogen bromide (HBr, Merck), 1,10-decanediol (≥99%, Aldrich), 1,10-dibromo decane (≥98%, Fluka) and quinone (≥98%, Fluka) were utilized without any additional treatment.

2.2 Characterizations

The ^{1}H-NMR (250 MHz) solution spectra were recorded on a Bruker NMR Spectrometer using $CDCl_3$ with TMS as an internal reference. Fourier transform infrared (FT-IR) spectra were obtained using a Perkin-Elmer FT-IR Spectrum One spectrometer. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC. Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns ($G2000H_{HR}$, $G3000H_{HR}$ and $G4000H_{HR}$), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 0.5 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards. Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 10°C min under nitrogen flow.

2.3 Preparation of Dibrominated Polystyrene (Br-PS-Br) by ATRP

In a 50 mL Schlenk tube CuBr (0.18 g, 1.3 mmol), PMDETA (271 μL, 1.3 mmol), 1,2-bis(bromoisobutry–loxy)ethane (45) as an initiator (0.23 g, 0.65 mmol) and styrene (30 mL, 260 mmol) were introduced. Three freeze-pump-thaw cycles were performed and the tube was stirred in oil bath at 90°C for 45 min. After the given time, the mixture was diluted with THF. Then the copper complex was removed out by passing through a neutral alumina column, and THF was removed by rotary evaporation. Precipitation of the polymer was performed in a ten-fold volume of methanol. The solid was then collected after filtration and drying at 40°C in vacuum overnight (conv.: 9%; $M_{n,th}$: 4075; $M_{n,NMR}$:4000; $M_{n,GPC}$: 4090; M_w/M_n:1.06).

^{1}H-NMR ($CDCl_3$): $\delta = 7.07$–6.58 (m, 5H, Ar), 4.39 (bs, 1H, Ph-CH-Br), 3.37 (m, 2H, CO-O-CH_2-CH_2-O-CO), 1.85-1.45 (m, 3H, CH_2-CHPh), 0.85 (bs, 6H, O-CO-C-$CH_3)_2$).

2.4 Synthesis of Diazido Terminated Polystyrene (N_3-PS-N_3)

Br-PS-Br (2.0 g, 0.5 mmol) was dissolved in 10 ml DMF and NaN_3 (0.33 g, 5.0 mmol) was added. The resulting solution was stirred overnight at room temperature and precipitated into methanol. The product was filtrated and dried in vacuum at 40°C (M_{nGPC}: 4150, M_w/M_n: 1.08).

^{1}H-NMR ($CDCl_3$): 7.07-6.58 (m, 5H, Ar), 3.93 (bs, 1H, Ph-CH-N_3), 3.37 (m, 2H, CO-O-CH_2-CH_2-O-CO), 1.85-1.44 (m, 3H, CH_2-CHPh), 0.85 (bs, 6H, O-CO-C-$CH_3)_2$).

IR (cm^{-1}): 3060, 3026, 2923, 2850, 2093, 1730, 1601, 1492, 1451, 755, 696.

2.5 Synthesis of 1,10-Diazido Decane (DAD)

A mixture containing 1,10-dibromo decane (2.0 g, 6.7 mmol) and sodium azide (4.3 g, 67 mmol) in 50 ml DMF was refluxed overnight. DMF is removed by means of vacuum distillation and subsequently the crude product was extracted with water and dichloromethane. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the product was attained as a yellowish liquid with 90% yield.

^{1}H-NMR ($CDCl_3$): 3.24 (t, 4H, -CH_2-N_3), 1.55 (m, 4H, -CH_2-CH_2-N_3), 1.28 (m, 12H, CH_2).

IR (cm^{-1}): 2930, 2853, 2084. 1683, 1452, 1341, 1257, 1082, 897, 740, 647.

2.6 Synthesis of 1,10-Dipropargyloxy Decane (DPD)

In a 250 ml two-neck round-bottom flask 1,10-decanediol (0.5 g, 2.9 mmol) was dissolved in 150 ml dry THF. NaH (1.5 g, 62.5 mmol) was added to solution. The flask and condenser were sealed with rubber stoppers. Propargyl bromide (7.4 g , 62.5 mmol) was added dropwise by using a syringe. The reaction apparatus was subjected to argon flow in order to prevent and get rid of traces of humidity and oxygen before and during reflux. The reaction mixture was stirred overnight at reflux temperature. After removal of the solvent, remaining part was extracted with dichloromethane and water. The organic layer was dried over anhydrous Na_2SO_4.After removal of the solvent, the remaining liquid was purified by column chromatography over silica gel with pure hexane. The product was obtained as a yellowish liquid after removal of hexane. Yield is 65%.

^{1}H-NMR ($CDCl_3$): 4.08 (d, 4H, -OCH_2CH), 3.46 (t, 4H, -CH_2OCH_2CH), 2.38 (t, 2H, -OCH_2CH), 1.55 (m, 4H, -CH_2-CH_2OCH_2CH), 1.25 (m, 12H, CH_2).

IR (cm^{-1}): 3305, 2923, 2850, 2112, 1455, 1355, 1264, 1091, 1018, 908, 809, 672, 635.

2.7 Synthesis of Dipropargyloxy Benzene (DPB)

Hydroquinone (2.0 g, 18.2 mmol) and of K_2CO_3 (5.5 g, 40 mmol) was mixed in 60 ml of acetone. Propargyl bromide (4.3 g, 36 mmol) was added dropwise to the mixture under argon atmosphere. Reaction was carried on overnight at reflux temperature. After removal of the solvent, the reaction mixture was extracted with dichloromethane and water. The organic layer was dried and removed dichloromethane. The product was obtained as pale yellow crystals after purification via column chromatography over silica gel with 9:1 hexane-ethyl acetate (yield: 72%).

^{1}H-NMR ($CDCl_3$): 6.92 (t, 4H, *aromatic*), 4.64 (d, 4H, $PhOCH_2CH$), 2.49 (t, 2H, -OCH_2CH).

IR (cm^{-1}): 3273, 2982, 2915, 2865, 2130, 1505,1377, 1211, 1025, 1011, 625, 785, 689.

2.8 Synthesis of Dipropargyloxy Triptycene (DPT)

Triptycene hydroquinone (10) (2.0 g, 7.0 mmol) and K_2CO_3 (2.1 g, 15 mmol) was mixed in 50 ml of acetone. Propargyl bromide (1.8 g, 15.4 mmol) was added dropwise to the mixture under argon atmosphere. Reaction was kept overnight at reflux temperature. The same workup described in DPB synthesis was applied to DPT. The product was achieved as pale yellow crystals with 65% yield.

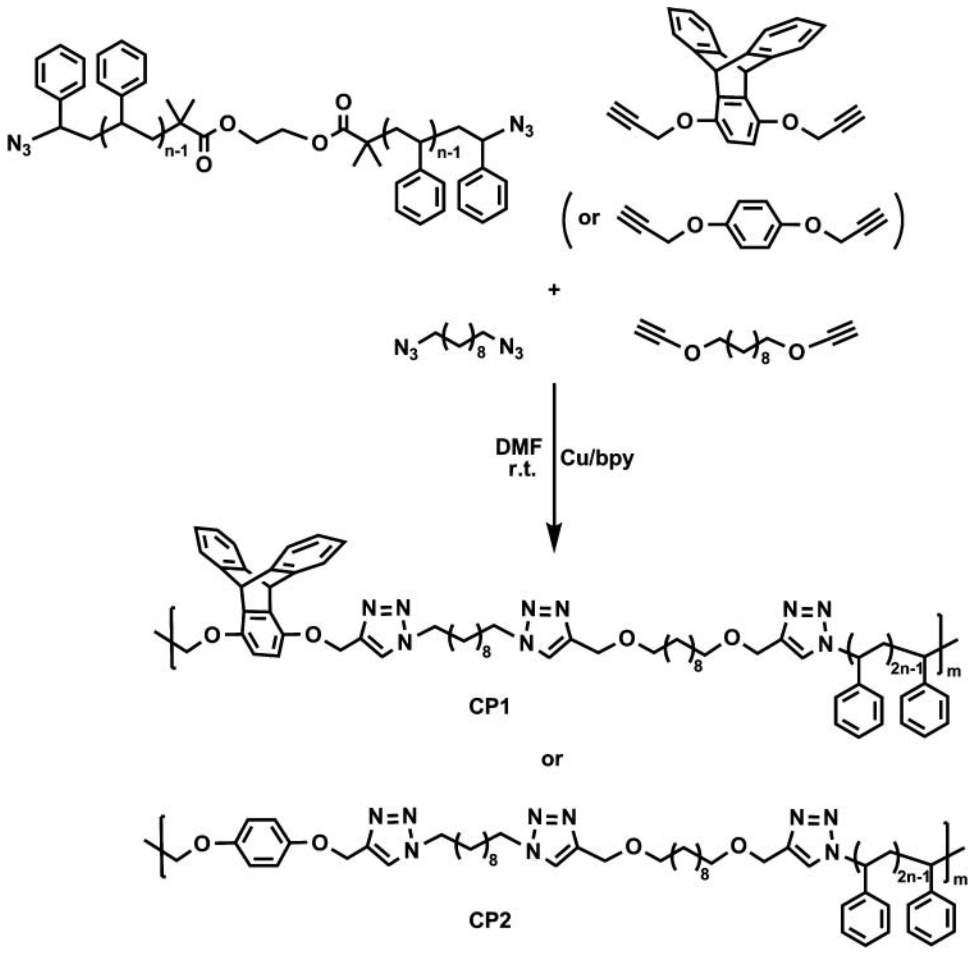
^{1}H-NMR ($CDCl_3$): 7.40 (q, 4H, *aromatic*), 6.96 (q, 4H, *aromatic*), 6.64 (s, 2H, *aromatic*), 5.87 (s, 2H, CH, *bridgehead protons*), 4.66 (d, 4H, -OCH_2CH), 2.48 (t, 2H, OCH_2CH).

IR (cm^{-1}): 3294, 3268, 2982, 2869, 2118, 1488, 1456, 1274, 1227, 1061, 915, 776, 728, 713, 665, 634.

2.9 Synthesis of Triptycene Containing Copolymer by Click Chemistry (CP1)

Triptycene containing click product (CP1) was synthesized in a Schlenk tube. CuBr (35 mg, 0.24 mmol) and PMDETA (51 μL, 0.24 mmol) and N_3-PS-N_3 (0.1 g, 0.024 mmol), DPT (8.8 mg, 0.024 mmol), DAD (22 mg, 0.098 mmol) and DPD (24 mg, 0.098 mmol) were mixed in dry DMF (4 mL) within the Schlenk tube. Two freeze-pump-thaw cycles were performed in order to get rid of oxygen inside the solution. Then, the degassed reaction mixture was stirred overnight at room temperature. After the reaction was ended, the mixture was diluted with THF. Then the copper complex was removed out by passing through a neutral alumina column, and THF was removed by rotary evaporation. Precipitation of the polymer was performed in a ten-fold volume of methanol. The solid was then collected after filtration and dried at 40°C in vacuum overnight.

^{1}H-NMR ($CDCl_3$): 7.50 (q, *aromatic*), 7.07-6.63- (*broad aromatic*), 5.82 (s, 2H, CH, *bridgehead protons*), 5.18 (s, 4H, triazole-CH_2−OCH_2−,), 5.02 (bs, 4H, triazole-CH_2−CHPh,), 4.61 (d, 4H, triptycene-O-CH_2−triazole), 4.31 (d, 4H, N-CH_2-$(CH_2)_8$), 3.50 (8H O-$CH_2(CH_2)_8$ and



Sch. 2. Overall process for copolymerization of azide terminated bifunctional polystyrene (N_3-PS-N_3) by "click" chemistry.

CO-O-CH_2-CH_2-O-CO), 1.87-1.27 (*broad aliphatic*), 0.86 (bs, 6H, O-CO-C-$CH_3)_2$).

IR (cm^{-1}): 3066, 3028, 2926, 2851, 2088, 1728, 1603, 1493, 1448, 1369, 1226, 1108, 1036, 752, 697.

2.10 Synthesis of Homologous Copolymer Without Triptycene by Click Chemistry (CP2)

The same synthesis route which was described for CP1 was applied to achieve hydroquinone containing click product (CP2). Equal amounts of the reactants and reagents were used except DPB (5.0 mg, 0.024 mmol) was received instead of DPT.

^{1}H-NMR ($CDCl_3$): 7.20-6.68- (*broad aromatic*), 6.28-6.68- (*broad aromatic*), 5.14 (s, 4H, triazole-CH_2-OCH_2-,), 5.02 (bs, 4H, triazole$-CH_2-$CHPh,), 4.61 (d, 4H, Ph$-$O$-CH_2-$triazole), 4.32 (d, 4H, N$-CH_2-(CH_2)_8$), 3.50 (8H, O$-CH_2(CH_2)_8$ and CO$-$O$-CH_2-CH_2-$O$-$CO), 1.87–1.27 (*broad aliphatic*), 0.86 (bs, 6H, O-CO-C-$CH_3)_2$).

IR (cm^{-1}): 3059, 3026, 2922, 2851, 2094, 1730, 1601, 1492, 1452, 1370, 1103, 1028, 907, 755, 696.

3 Results and Discussion

The synthetic strategy involving combination of ATRP and click chemistry, applied for the preparation triptycene containing polystyrene is outlined in Scheme 2. Well-defined precursor polystyrene with predetermined molecular weight and narrow polydispersity was prepared by ATRP in the presence of Cu(I)/PMDETA catalyst system. Bromine terminal groups of polystyrene were converted to azide group by using NaN_3. As another component of click reaction, alkyne containing compounds were synthesized by simple etherification reaction with propargyl bromide. Azide and alkyne containing alkyl chain were also prepared in order to facilitate threading of the polymer chains through triptycene cavities.

Triptycene units were introduced into copolymer via click reaction using Cu(I) catalyst in DMF and compared to the homologous copolymer without triptycene (Sch. 2). The formation of triptycene containing copolymers (CP1) was investigated using

^{1}H-NMR, FT-IR and GPC. ^{1}H-NMR spectrum of CP1 obtained by click reaction indicated characteristic peaks of all components (Fig. 1). While alkyne protons of

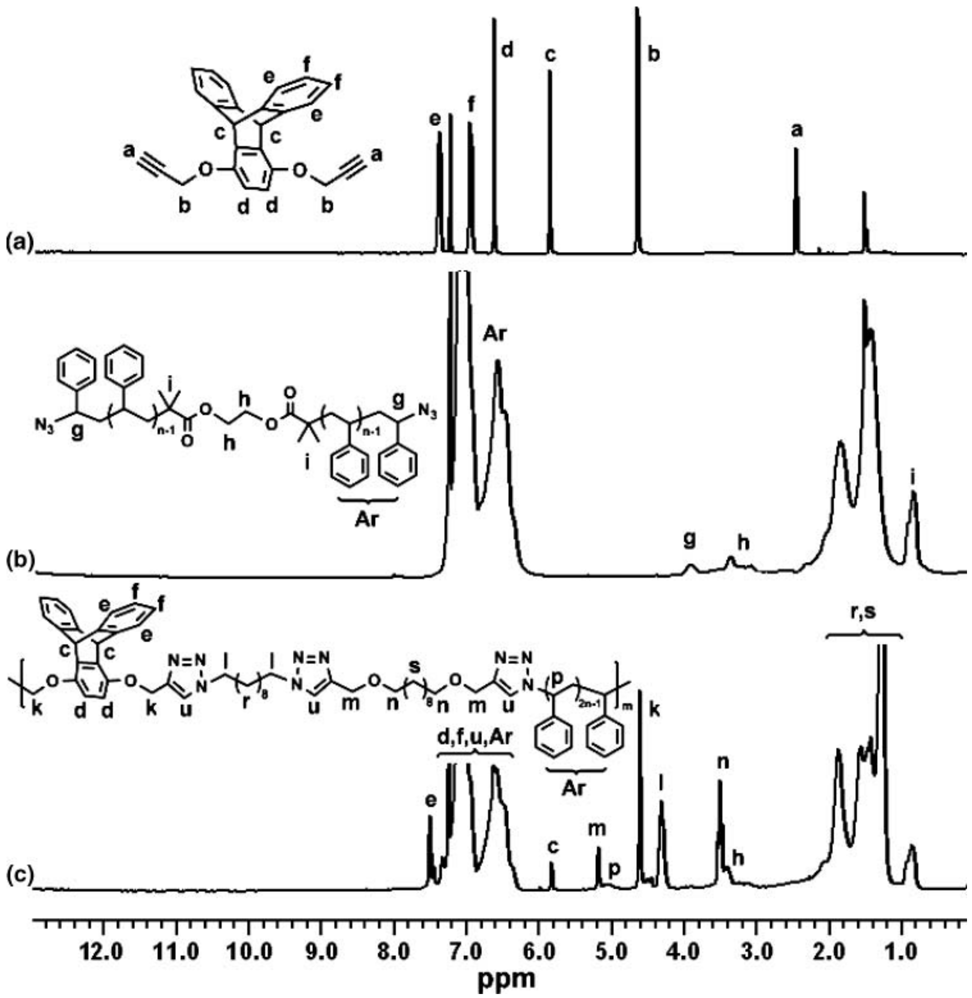


Fig. 1. ^{1}H-NMR spectra of dipropargyloxy triptycene (DPT) (a), azide terminated bifunctional polystyrene (N_3-PS-N_3) (b), and triptycene containing copolymer (CP1) (c) in $CDCl_3$.

triptycene (a protons in Figure 1a) and end group protons of azide terminated polystyrene (g protons in Figure 1b) completely disappeared, the new signal corresponding to methylene and methine protons (p,m,l,k protons in Figure 1c) linked to triazole rings were observed at between 5.18 and 4.31 ppm. Also, some aromatic protons of triptycene unit (e protons in Figure 1a) were clearly observed in the spectrum of copolymer (Fig. 1c). The characteristic bridgehead protons of triptycene observed at 5.87 ppm (c protons in Figure 1a) were detectable in the corresponding copolymer spectrum at 5.82 ppm (c protons in Figure 1c). Although the sequences of the aliphatic and aromatic propargyl molecules are irregular, these results indicate that composition of the resulting polymer is in agreement with the feed ratio of the click components in coupling process (see Experimental section).

The conversion of the click reaction and molecular weight characteristics together with the thermal properties of CP1 and homologous copolymer without triptycene (CP2) are displayed in Table 1. In both cases, the

Table 1. Molecular weight characteristics of the polymers and their thermal properties

				Thermal Properties	
Code	*Conv.*[a] *(%)*	M^b_{nGPC}*(g/mol)*	M_w/M^b_n	T^c_g	$T^d_{deg}(T_{ini,deg})$
CP1	82	20400	1.44	69.7	399 (255)
CP2	76	15750	1.21	61.7	394 (237)

Starting polystyrene (Br-PS-Br); M_{nGPC}: 4090, M_w/M_n: 1.07 and N_3-PS-N_3 M_{nGPC}: 4150, Mw/M_n: 1.08.

[a] Determined by gravimetrically.

[b] Determined from GPC measurements based on polystyrene standard. M_n: the number average molecular weight, M_w: the weight average molecular weight.

[c] The glass transition temperature (T_g) of copolymers was determined by using DSC. T_g of Br-PS-Br was determined as 81.4°C.

[d] The degradation temperature (T_{deg}) of copolymers was determined by using TGA. $T(_{ini,deg})$ is initial degradation temperature.

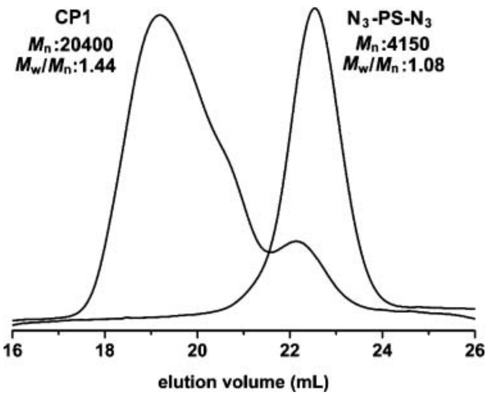


Fig. 2. GPC traces of starting polystyrene (N_3-PS-N_3), and triptycene containing copolymer (CP1).

molecular weight of the polymers increased significantly after the click coupling reaction. The increase is slightly higher in the case of triptycene polymer probably due to the additional molecular weight associated with the triptycene unit itself. In this connection, it should be pointed out that the final polymer contained about 10% of relatively low molecular weight polymer (c.a. M_n =5500). This polymeric product may form the coupling reactions of the low molar mass click components as its molecular weight value is slightly higher than that of the initial polystyrene. Because of the similar solubility properties, this product could not be removed by extracting with a selective solvent.

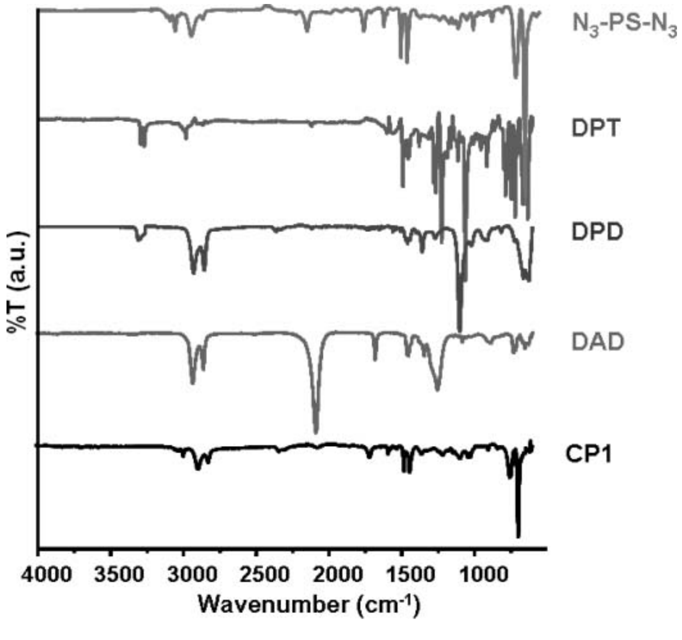


Fig. 3. FT-IR spectra of bifunctional azide terminated polystyrene (N_3-PS-N_3), dipropargyloxy triptycene (DPT), dipropargyloxy decane (DPD), diazido decane (DAD) and triptycene containing copolymer (CP1).

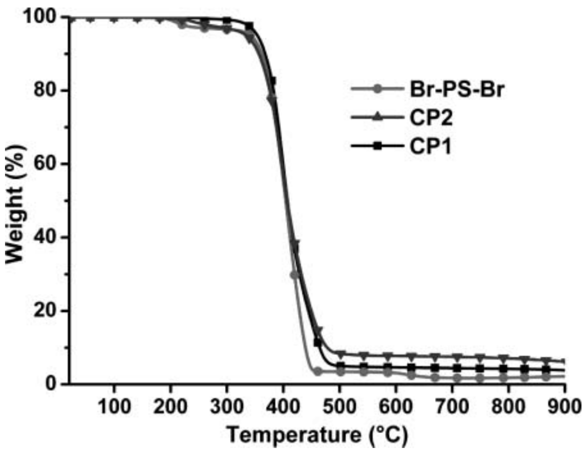


Fig. 4. TGA curves of starting polystyrene (Br-PS-Br), triptycene containing copolymer (CP1) and homologous copolymer without triptycene (CP2).

The precursor polymer and the final copolymer were also analyzed by FT-IR spectroscopy and expected structures were confirmed. As can be seen from Figure 3, the vibrations of the azide group at the end of the polystyrene and diazidodecane structure were observed at 2099 cm^{-1}. Similarly, the vibrations of the azide and C-H groups and triple bonds of alkyne groups in the dipropargyloxy triptycene and dipropargyloxy decane structures were also noted at around 2110 cm^{-1}. As a result of click coupling between these components, the vibrations of the azide and alkyne groups disappeared in the spectrum of CP1.

The thermal properties of copolymers were measured by TGA and DSC. As shown by the TGA curve (Fig. 4), the decomposition of CP1 and CP2 were observed around 400°C under a nitrogen atmosphere. CP1 exhibits slightly better thermal properties than Br-PS-Br and CP2.

Figure 5 displays the DSC trace of starting polystyrene and copolymers. Low molecular weight Br-PS-Br shows a

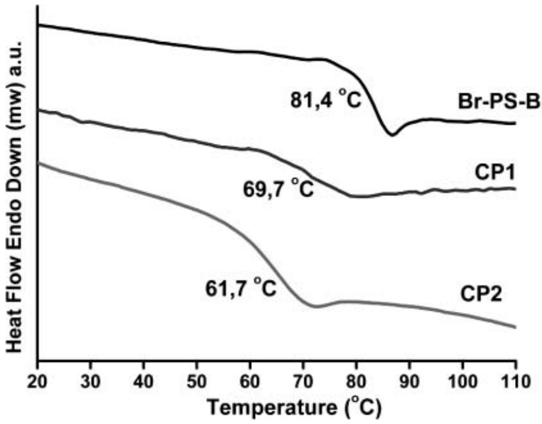


Fig. 5. DSC traces of starting polystyrene (Br-PS-Br), triptycene containing copolymer (CP1) and homologous copolymer without triptycene (CP2).

typical glass transition temperature (T_g) at 81.4°C. As a reference polymer CP2 shows a lower T_g at 61.7°C than the precursor polymer due to the presence of additional alkyl chain in the polymer. Although CP1 contains the same alkyl chain in the structure, it exhibits a higher T_g (69.7°C) value because the triptycene units stiffened the chain backbone.

4 Conclusions

In conclusion, in this paper we reported synthesis of polystyrene possessing triptycene moiety in the structure by combination of ATRP and "click" chemistry. The intermediates and the resulting polymers were caharacterized by spectral and thermal analyses methods. The effect of the triptycene moiety on the thermal properties was demonstrated. In the light of present study and the general behavior of triptycene molecules in polymer chains it is expected that polymers with enhanced properties such as ductility and stiffness can be obtained by ATRP combined with "click" chemistry. Further studies on the investigation of these properties are now in progress.

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