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Synthesis and Characterization of Polysulfone-based Graft Copolymers Possessing Quaternary Ammonium Salts via Photoiniferter Polymerization

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Abstract: Well-defined polysulfone-based graft copolymers containing quaternary ammonium salts were successfully prepared by photoiniferter method under mild conditions (at room temperature and nitrogen atmosphere). The corresponding macroiniferter agent was sequentially synthesized by chloromethylation and nucleophilic substitution reactions between obtained chloromethylated polysulfone and sodium diethyldithiocarbamate. Upon UV irradiation, this macroiniferter enabled the accomplished grafting of 2-(dimethylamino) ethyl methacrylate onto the polysulfone backbone in a controlled manner. After the successful synthesis of graft copolymers, the tertiary amine groups in the side-chains are readily quaternized using methyl iodide to get desired quaternary ammonium salts containing graft copolymers.

Keywords*:* Graft copolymer; iniferter; polysulfone; photopolymerization; quarternary ammonium salts.

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INTRODUCTION

Polysulfones (PSU) are the family of thermoplastics that have excellent thermal and chemical stability, high radiation degradation resistance, transparency, high rigidity, mechanical strength, and good electrical and film properties (1, 2). To benefit from above-mentioned advantages, they have been used in many applications such as medical devices (hemodialysis), food processing, feeding systems, automotive, electronics, water distillation, gas separation, and fuel cells (3-5). However, these PSU have some drawbacks including stress cracking with certain solvents, poor tracking resistance, and weathering properties. To overcome these limitations and also extend their potential applications, the functionalization of PSU is a subject of considerable interest in recent studies (6, 7). There are two main functionalization methods; (i) functional monomer and (ii) post-functionalization approaches (8). The post-functionalization is most widely applied method in which the desired functionality is attached onto the polymer end- or side-chains of polymers (9, 10). The chemical structure of PSU backbone contains two different repeating units, electron-deficient phenyl sulfone and electron-rich bisphenol A groups that are suitable both electrophilic and nucleophilic substitution reactions for the incorporation of various functional groups. For example, sulfonation, chloromethylation, lithiation, and other methods are successfully applied for the side-chain functionalization of PSU in the literature (9). The grafting method including polymer chains with different chemical natures are attached onto another polymer backbone is a versatile process for the functionalization of polysulfones (11-16). The resulting functional polysulfone graft copolymers exhibit superior properties such as high porosity, wettability, and protein resistance compared to the non-functionalized polysulfones.

The iniferter (initiator-transfer-terminator agent) polymerization is the first controlled radical polymerization method discovered by Otsu and co-workers (17-19). In this method, the radical polymerization proceeds in a controlled manner where “active” and “dormant” propagating chain ends are reversibly equilibrated throughout the polymerization period (20-22). Various macromolecular architectures including telechelic (23, 24) and hyper-branched polymers (25, 26) and also block (27-31) and graft (32) copolymers can be simply synthesized under mild conditions via thermal or photochemical activations.(33, 34)

In this study, firstly, commercially available polysulfone was chloromethylated by a well-known procedure using paraformaldehyde, trimethylsilyl chloride, and tin (IV) chloride. Then, the obtained polymers were converted to the macroiniferter by changing chloromethyl moieties with diethyl dithiocarbamate groups via nucleophilic substitution reaction. By applying UV irradiation, this macroiniferter (side-chain functional diethyl dithiocarbamate polysulfone) were enabled to conduct the radical polymerization of 2-(dimethylamino) ethyl methacrylate in a controlled manner. As a result of the iniferter polymerization, a well-defined graft copolymer (polysulfone-*g*-poly(2-(dimethylamino)ethyl methacrylate)) was successfully synthesized under mild conditions, *i.e.,* UV irradiation and room temperature. Finally, quaternization experiment using methyl iodide was applied to obtain desired polysulfone graft copolymer containing quaternary ammonium salts. The structures and properties of intermediate and final products were characterized by various techniques including spectroscopic (FT-IR and ^{1}H-NMR), chromatographic (GPC), and thermal (DSC) analysis.

MATERIALS AND METHODS

Materials

Polysulfone (Udel® P-1700, Solvay), paraformaldehyde (95%, Merck), tin(IV) chloride (98%, Alfa Aesar), trimethylsilyl chloride (≥ 99.0%, Aldrich), sodium azide (99%, Merck), sodium diethyldithiocarbamate (BDH Chem.) 2-(dimethylamino)ethyl methacrylate (99%, Merck) and methyl iodide (Aldrich) were used as received. Commercial grade solvents *N,N*-dimethylformamide (≥ 99.8%, Merck), chloroform (≥ 99.8%, Merck), pyridine (≥ 99.0%, Aldrich), dimethyl sulfoxide (VWR) tetrahydrofuran (≥ 99.7%, VWR) and methanol (100%, VWR) were purchased and used as received.

Chloromethylation of polysulfones

Polysulfone (20 g, 0.5 mmol) was dissolved with chloroform (600 mL) in a 1000 mL glass flask by using ultrasonic bath and then paraformaldehyde (57 mL, 450 mmol) and trimethylsilyl chloride (57 mL, 450 mmol) were added carefully into the mixture (13). After the mixture was stirred for a while, tin(IV) chloride (0.52 mL, 4.5 mmol) was added into this solution and the mixture was stirred at room temperature for 72 hours. All these steps and the reaction were carried out under inert atmosphere. End of the given time, the product was precipitated into excess methanol. Then, the precipitate was filtered and dried in a vacuum oven at room temperature.

In order to confirm the successful of the chloromethylation process by FT-IR spectroscopy, the chloromethyl groups were converted to azide groups having characteristic band at 2150 cm^{-1}. For this purpose, the chloromethylated polysulfone (PSU-CH_2-Cl) (1 g, 0.026 mmol) was dissolved in 20 mL of dimethylformamide (DMF) and sodium azide (NaN_3) (100 mg, 1.54 mmol) was added into the solution. The mixture flask was wrapped up with alumina film to protect from solar light and then the mixture was stirred at 50 ^{0}C for 24 h. Finally, the product was precipitated into excess methanol, filtered, and dried in a vacuum oven at room temperature.

Synthesis of polysulfone-based macroiniferter (PSU-DDC)

Iniferter functionalized polysulfone (PSU-DDC) was synthesized from the reaction of PSU with sodium diethyldithiocarbomate (35). The PSU-CH_2-Cl (500 mg, 0.013 mmol), sodium diethyldithiocarbamate (60 mg, 0.35 mmol) and pyridine (5 mL) were placed to a 100 mL flask. After mixing and dissolution processes had been finished, the mixture flask was stirred in silicon oil bath at room temperature for 24 h. The solution was precipitated into methanol, filtered, and dried in a vacuum oven.

Synthesis of polysulfone-g-poly(2-(dimethylamino)ethyl methacrylate) (PSU-g-PDMAEMA) via photoiniferter polymerization

PSU-DDC (50 mg, 0.0013 mmol) and DMF (1 mL, 0.013 mmol) were placed into a tube. After PSU-DDC completely dissolved, 2-(dimethylamino)ethyl methacrylate (DMAEMA) (1 mL, 5.94 mmol) was added into the solution tube and nitrogen was bubbled through 2-3 minutes. Then, the tube was irradiated by a UV photoreactor within 300-400 nm wavelength (Philips TL-D 18W) at room temperature for different reaction times. The solution mixture was precipitated into excess amount of hexane and then filtered. The product was dried under vacuum.

Quarternarization of PSU-g-PDMAEMA

PSU-g-PDMAEMA (165 mg, 0.003 mmol) and THF (5 mL, 0.07 mmol) were added into a flask. After the polymer was completely dissolved, methyl iodide (CH3I) (50 µL, 0.0008 mmol) was carefully added into the solution flask and the mixture was stirred in silicon oil bath at room temperature for 24 h. The mixture was precipitated in hexane and filtered. After filtration, polymers were dried for 24 hours in a vacuum oven.

Analysis

A Perkin-Elmer FT-IR Spectrum One B spectrometer was used for FT-IR analysis. The Agilent NMR System VNMRS 500 spectrometer was used at room temperature in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard for ^{1}H-NMR analysis. Molecular weights were determined by a Viscotek GPCmax Autosampler system consisting of a pump module (GPCmax, Viscotek, Houston, TX), a combined light-scattering (Model 270 dual detector, Viscotek), and a refractive index (RI) detector (VE 3580, Viscotek). The light-scattering detector (λ_0=670 nm) included two scattering angles: 7 and 90°. The RI detector was calibrated with polystyrene standards having narrow molecular weight distribution, and hence the quoted molecular weights of the polymers were expressed in terms of polystyrene equivalents. Two columns (7.8 x 300 mm, LT5000L, Mixed, Medium Org and LT3000L, Mixed, Ultra-Low Org) with a guard column (4.6 x 10 mm, Viscotek, TGuard) were used for the chloroform eluent at 35 ^{0}C (flow rate, 1 mL/min). Data were analyzed using Viscotek OmniSEC Omni-01 software. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC with a heating rate of 10 ^{0}C/min under nitrogen flow (10 mL/min).

RESULTS AND DISCUSSIONS

There are three main methods for the synthesis of graft copolymers; (i) grafting-onto, (ii) grafting-from and (iii) grafting-through (macromonomers) (36-39). Among them, grafting-from approach is a very useful method since a wide range of monomers can be used together with different reaction conditions (40). In this method, an initiator is attached onto the polymer backbone and subsequent polymerization of second monomer enables to form corresponding graft copolymers. In our case, firstly, iniferter (diethyl dithiocarbamate) group was attached onto PSU backbone by sequantial chloromethylation and nucleophilic substitution reactions. The chloromethylated polysulfone was synthesized according to the well-known procedure (13). Then, its structure was confirmed by FT-IR and ^{1}H-NMR techniques in accordance with respect to the literature data (11, 15). Due to overlapping of chloromethyl bands with the characteristic polysulfone bands, determination of chloromethylation was difficult with FT-IR spectroscopy. Therefore, the chlorine atoms were replaced with azide groups that were easily detectable in FT-IR spectroscopy. The characteristic azide band at 2250 cm^{-1} was obviously detected in FT-IR spectrum (Figure 1). Thus, the successful chloromethylation of PSU was proven by FT-IR spectroscopy.

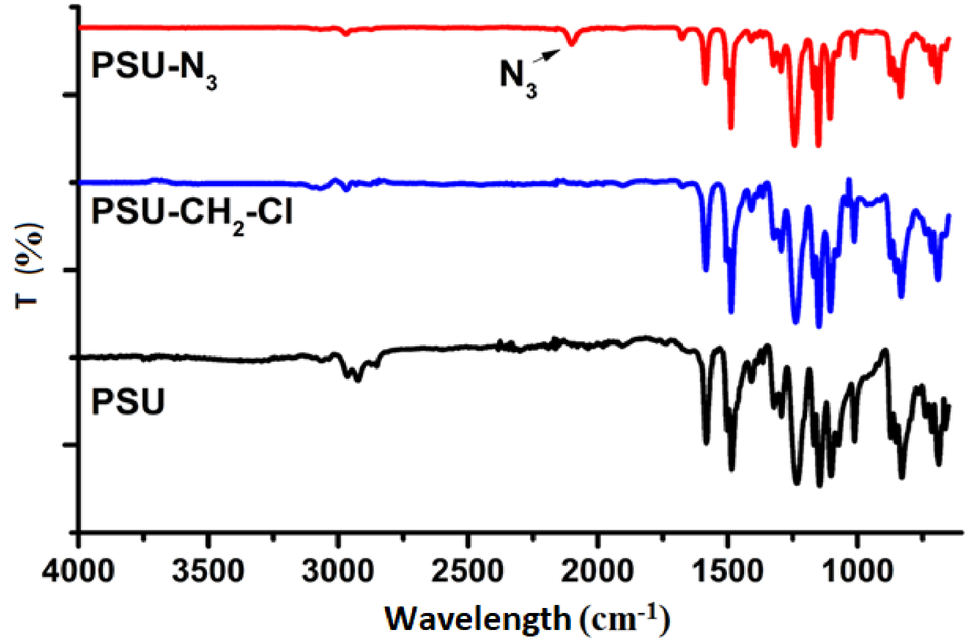


Figure 1. FT-IR spectra of neat, chloromethylated- and azide-functionalized polysulfones.

The successful transformation as well as the degree of substitution of chloromethyl group in PSU were determined by ^{1}H-NMR measurement. As can be seen in Figure 2, six methyl protons (a) and two methylene protons (b) of PSU-CH_2Cl appeared at 1.7 and 4.6 ppm, whereas four aromatic protons (c) were detected at 7.9 ppm. The degree of substitution of chloromethyl group into PSU backbone was calculated by using integral ratio of b and c protons and it was found as 7%.

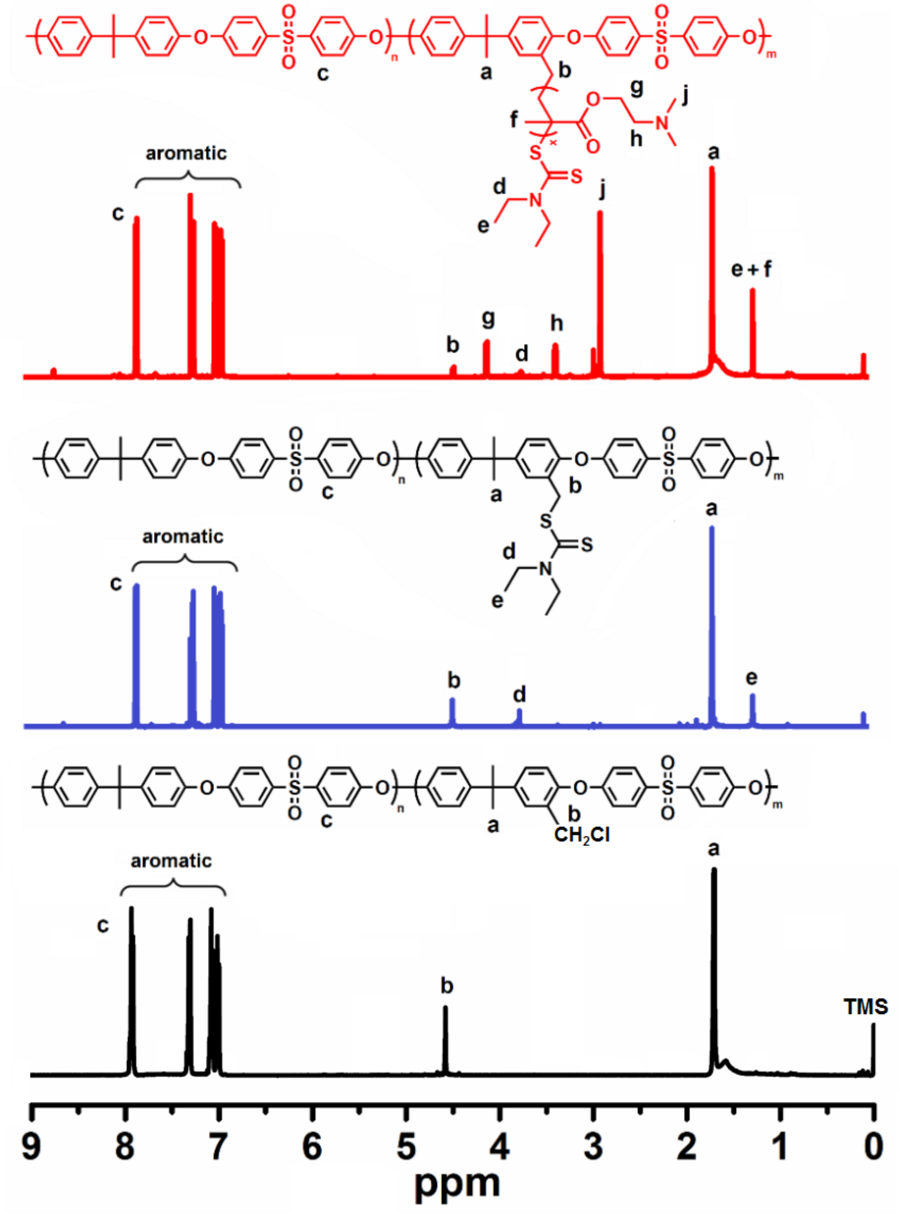
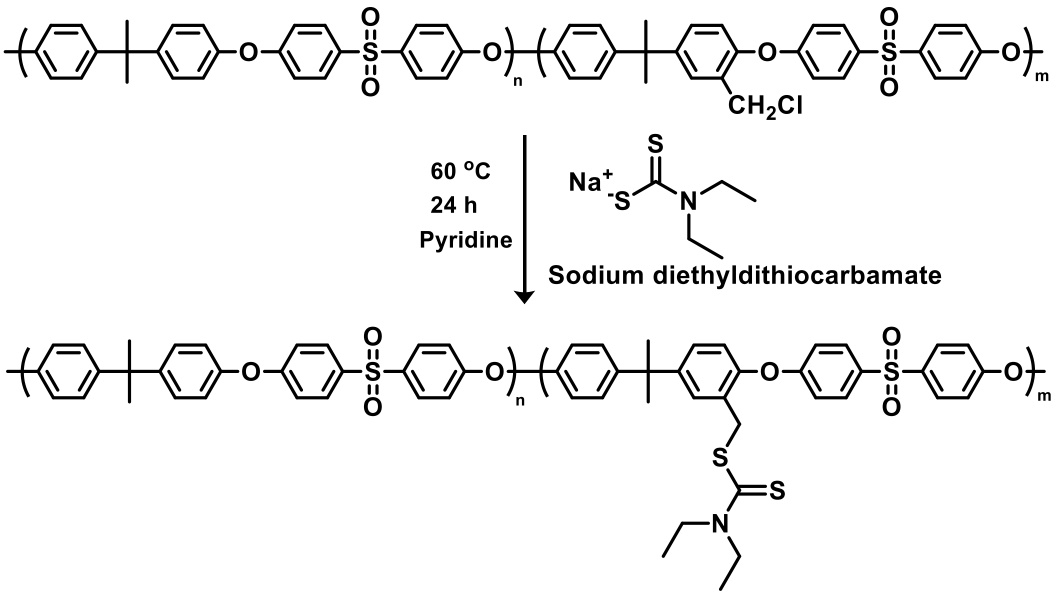


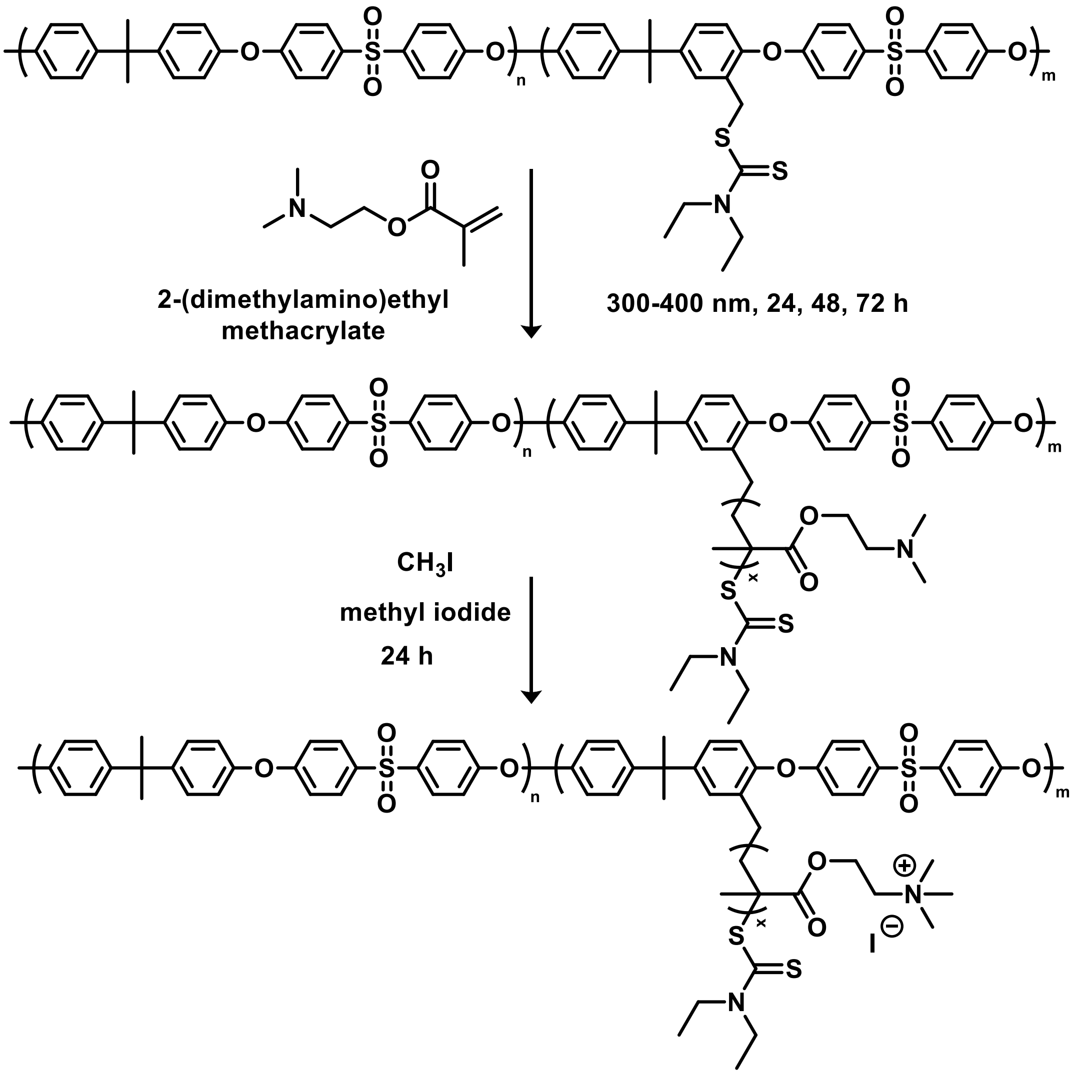
Figure 2. ^{1}H-NMR spectra of PSU-CH_2Cl, PSU-DDC and PSU-*g*-P DMAEMA.

In the second step, the macroiniferter (polysulfone containing diethyl dithiocarbamate) was prepared by nucleophilic substitution reaction of PSU-CH_2Cl and sodium diethyl dithiocarbamate according to Scheme 1. The chemical structure of PSU-DDC was monitored by ^{1}H-NMR spectroscopy. As can be seen in Figure 2, six methyl (e) and four methylene (d) protons of DDC moieties were observed at 1.3 and 3.8 ppm. In addition, the characteristic peaks of methyl (a), methylene (b) and aromatic protons (c) were observed at the same regions. These results clearly confirmed the successful transformation from PSU-CH_2Cl to PSU-DDC.



Scheme 1. The synthesis of macroiniferter agent (PSU-DDC).

Upon UV exposure, the PSU-DDC macroiniferter generated two types of radicals, an active radical on the PSU backbone and an inactive radical (DDC•). While the active macroradicals could initiate the polymerization of 2-(dimethylamino)ethyl methacrylate (PDMAEMA), the inactive radicals allowed to control the chain growth by eliminating unreversible termination reactions to obtain well-defined PSU-*g*-PDMAEMA graft copolymers (Scheme 2).



Scheme 2. The synthesis of PSU-*g*-PDMAEMA and PSU-*g*-QPDMAEMA.

By changing polymerization time, a series of graft copolymers was obtained and their structures were confirmed by FT-IR and ^{1}H-NMR analyses. As shown in Figure 3, the characteristic ester peaks of C=O and C-O-C of PDMAEMA were sharply observed at 1712 and 1100 cm^{-1}, whereas the –N(CH)$_3$, –CH and C-C-N bands were seen at 2825, 2775 and 1160 cm^{-1}. In addition, the aromatic C=C streching bands of PSU units were displayed at 1590 and 1485 cm^{-1}. The graft copolymer structures were also investigated by ^{1}H-NMR spectroscopy. Both the aliphatic (a) and aromatic (c) peaks belonging to protons of PSU backbone were clearly appeared at the same region. The new peaks assigned to aliphatic (j,h,g and f) -CH$_2$ and -CH$_3$ protons of PDMAEMA blocks appeared at

2.9, 3.4, 4.1 and 1.5 ppm, respectively. Additionally, the methyl protons of DDC groups were still visible after graft copolymerization as shown in Figure 2.

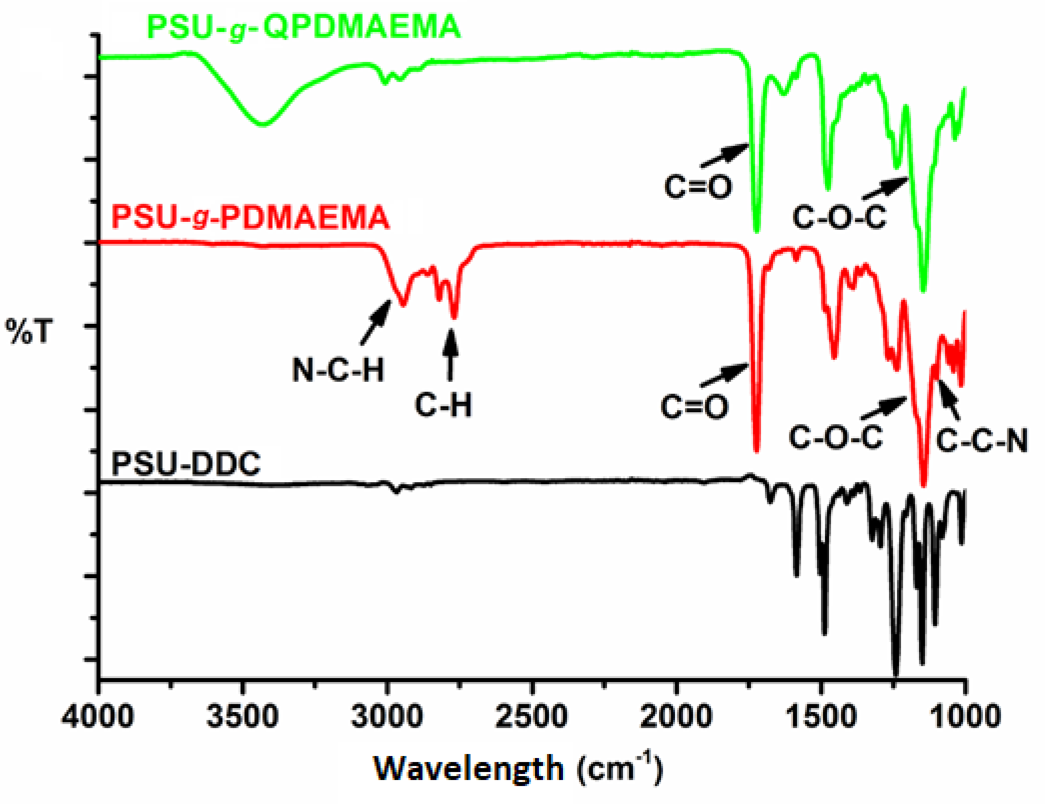


Figure 3. FT-IR spectra of PSU-DDC, PSU-*g*-PDMAEMA and PSU-*g*-QPDMAEMA.

The compositions of obtained graft copolymers were determined from the integration ratio of the protons (**c** and **j**) belonging to PSU and PDMAEMA blocks by using ^{1}H-NMR spectroscopy. As a results, the conversions as well as the molecular weights of graft copolymers were gradually increased by increasing the polymerization time. In contrast, the composition of PSU segments in the graft copolymers were paralelly decreased from 68 to 35% (Table 1).

Molecular weight distributions of inital PSU and obtained graft copolymers were investigated by gel permeation chromatography. The peaks belonging to graft copolymers were shifted to lower retention times meaning higher molecular weights than neat PSU backbone. After 72 h grafting process, the molecular weight was shifted from 38.000 g/mol to 121.000 g/mol (Table 1). Furthermore, all graft samples displayed single GPC peak accompanied by relatively narrow molecular weight distributions below 2.10. This result implied that it was not admixed with an independently formed homopolymer. The single GPC peaks indicated that was no homopolymer contamination of graft copolymerization (Figure 4).

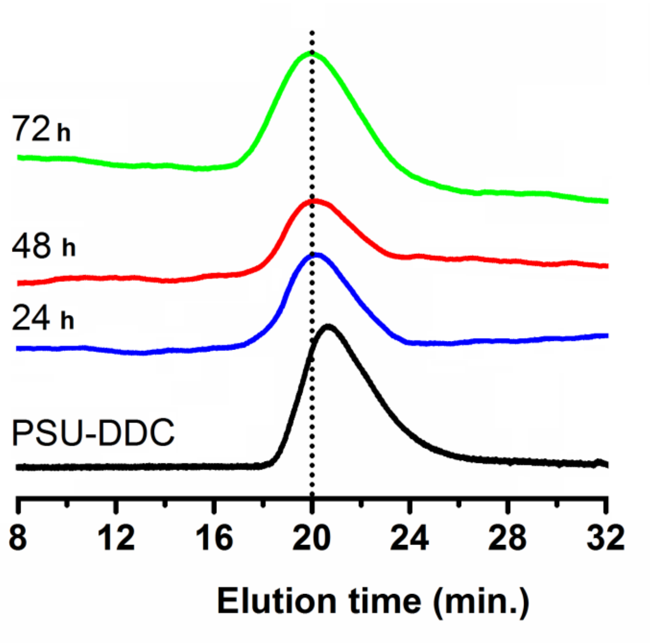


Figure 4. GPC curves of PSU-DDC and PSU-*g*-PDMAEMA polymers.

The thermal properties of resulting graft copolymers (PSU-g-PDMAEMA) were investigated by DSC analysis under nitrogen atmosphere and compared with initial PSU-DDC sample. According to DSC analysis, The PSU-DDC displayed a glass transition temperature (T_g) around 185 °C. The obtained graft copolymers were displayed only single T_g values at between 105 and 123 °C. In the literature, the T_gs of neat PSU and PDMAEMA were determined around 190 and 5 °C, respectively.(40, 41) The T_gs of graft copolymers decreased from 123 to 105 ^{0}C by increasing composition of PDMAEMA segments (Table 1).

Table 1. The characterization results of PSU-DDc and PSU-g-PDMAEMA polymers.

Polymer	**[Inf]/ [M]**	**Time (h)**	**$M_{n,GPC}$ (g/mol)^a**	**M_w/ M_n^{a}**	**Yield (%)^b**	**Comp. (%)^c**	**T_g (°C)^d**
PSU-DDC	-	-	38.000	1.74	95	100	185
PSU-*g*-PDMAEMA-24	1/760	24	53.000	1.58	47	68	123
PSU-*g*-PDMAEMA-48	1/760	48	96.000	1.75	67	43	112
PSU-*g*-PDMAEMA-72	1/760	72	121.000	2.10	98	35	105

[a)]Determined by GPC, [b)]Calculated gravimetrically, [c)]Determined by ^{1}H-NMR spectroscopy from the intagration ratio of the protons (**c** and **j**), [d)]Measured by DSC under nitrogen atmosphere.

After the successful grafting process, the tertiary amine groups in the graft copolymers were quaternized using methyl iodide to get corresponding quaternary ammonium salts containing graft copolymers (PSU-*g*-QPDMAEMA) (Scheme 2). Because of the solubility problems of quaternized graft copolymers, the ^{1}H-NMR spectroscopy and GPC analysis were not performed. The quaternization process was only characterized by using FT-IR spectroscopy. The PSU-*g*-PDMAEMA displayed the characteristic $–N(CH)_3$, –CH and C-C-N bands at 2825, 2775 and 1160 cm^{-1}, respectively. After quaternization process, the bands at 2825 and 2775 cm^{-1} of the PDMAEMA segments clearly disappeared. This result confirmed the successful formation of quaternary ammonium salts containing graft copolymers.

CONCLUSIONS

In conclusion, the PSU-based macroiniferter was successfully synthesized and applied for the polymerization of DMAEMA under mild conditions. This process allowed the successful synthesis of well-defined graft copolymers with high yields. The obtained graft copolymers displayed a single GPC peak with relatively narrow molecular weight distributions. The compositions of PDMEMA segments in the graft copolymers were gradually increased with increasing monomer conversion. All graft copolymers exhibited single T_g value at between 105 and 123 °C. After the successful synthesis of PSU-g-PDMAEMA, the tertiary amine groups in the side chains were readily converted to quaternary ammonium salts to obtain desired quaternary ammonium salts containing graft copolymers.

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