



Synthesis of Poly(styrene)-*g*-Poly(oleic acid) Graft Copolymers via Reversible Addition/Fragmentation Transfer (RAFT) Polymerization Using a Poly Oleic Acid Macro-RAFT Agent

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Abstract

In this study, a new polymeric oleic acid-derived macro addition/fragmentation transfer agent was utilized to produce a poly(styrene)-*g*-poly(oleic acid) graft copolymer. The double bond of oleic acid was initially saturated with bromine and the condensation polymerization between the carboxylic acid and the bromide resulted in polyoleic acid with pendant bromide groups. Xanthate groups were exchanged with the bromide groups to obtain the poly(oleic acid) macro RAFT agent (Pole-Xa). Poly(styrene)-*g*-poly(oleic acid) (PS-*g*-Pole) graft copolymers were synthesized via reversible addition fragmentation transfer (RAFT) polymerization of styrene and the reaction was evaluated in view of the polymerization kinetics. The effects of polymerization temperature and reaction time on graft copolymer yield, conversion and molecular weight were investigated. In the RAFT polymerization of styrene, the rate constant (*k*) was found to be 1.83×10^{-3} L/mol/dk and 7.27×10^{-4} L/mol/dk for the polymerization temperatures of 80 and 90 °C, respectively. The structural characteristics and thermal properties of the obtained products were characterized using FT-IR, ¹H-NMR, GPC, TGA, DSC and SEM-EDX.

Keywords Brominated oleic acid · Polymeric oleic acid · Graft copolymer · Polymerization kinetics

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Introduction

Controlled/living polymerization techniques such as nitroxide-mediated radical polymerization (NMP) [1–3], atom transfer radical polymerization (ATRP) [4–9], reversible addition fragmentation transfer (RAFT) polymerization and anionic polymerization are established techniques for copolymer synthesis. Among these techniques, RAFT, which was first introduced by Rizzardo et al. [10] and based on radical polymerization, has been successfully utilized in the synthesis of many types of block/graft copolymers due to the easy polymerization conditions using various chain transfer agents (CTA). In RAFT polymerization, the control of polymer molecular weight is provided by the specific chain transfer agents (CTA) used in the reaction. Xanthates are the preferred CTA agents because they are inexpensive and readily available. In this study, xanthate-mediated RAFT polymerization was utilized because of its easy applicability and mild polymerization conditions. [10–23].

Vegetable oil-based polymers (VOP) are attractive among biomaterials because they are derived from renewable resources that are inherently biodegradable and show low toxicity. Typically VOP are synthesized by taking advantage

of the carbon–carbon double bonds associated with the individual fatty acids that make up the oil or in certain circumstances the functional groups associated with the fatty acids. These may include hydroxyl groups as in ricinoleic acid or lesquerolic acid or epoxy groups as in vernolic acid. Depending on the reaction conditions, VOP have been synthesized with a variety of material properties ranging from soft and flexible rubbers to hard and rigid thermoplastics [24]. Oleic acid is one fatty acid that is found naturally and abundantly in various animal fats and vegetable oils. It is an odorless, colorless oil that is chemically classified as a monounsaturated omega-9 fatty acid that, because of its acrylic double bond, can be utilized as an important raw material for obtaining active-ended chemicals. It can be easily reacted to yield polymeric macroinitiators which can then be used to synthesize block/graft copolymers by connecting different monomers to their active sites due to the active centers at the chain ends of polymeric macroinitiators [25–34].

The importance of graft copolymers is gradually increasing, with numerous studies reporting from synthesis to application every year. Graft copolymers have been extensively studied due to their intriguing properties that are inherently different compared to their linear counterparts, and their importance as a macromolecular structure has been highlighted [35, 36]. The methods of preparation of such polymers are of interest because the properties of graft copolymers are different from the homopolymers of the monomers from which they are formed. Although a graft copolymer obtained from a single polymerization method is known to allow for facile synthesis, the combination of two different polymerization techniques can be an advantageous way to incorporate classes of monomers that may be incompatible [8, 27, 37].

In this study, graft copolymers were prepared by grafting PS onto the active centers of the Pole chains using two different techniques such as condensation and RAFT polymerization. Macropolymeric oils were synthesized by condensation polymerization to obtain graft copolymers via RAFT polymerization. The basis of this study was to prepare oil polymers, which are a natural product, and to report the synthesis of new partially biodegradable polymers by attaching a naturally biodegradable oil polymer to vinyl polymer such as polystyrene (PS) using graft copolymer synthesis.

Polystyrene (PS) is a petroleum-based polymer produced by the polymerization of styrene. At room temperature polystyrene is a solid thermoplastic with a high melting temperature (~240 °C) when processed by injection or extrusion. There have been many well-known polystyrene-containing block/graft copolymers in the literature. For example, Tuzen et al. [38] obtained and evaluated poly(styrene)-co-2-vinylpyridine by the reversible addition fragmentation chain transfer (RAFT) polymerization of styrene and 2-vinylidene. Rajendran et al. [39] using a styrene-based macro-RAFT

agent, produced polystyrene-graft-polymethyl methacrylate (PS-g-PMMA), polystyrene-graft-poly(isobornyl acrylate), polystyrene-graft-poly[2(acetoacetoxy)ethyl methacrylate] (PS-g-PAEMA), and poly(paramethoxystyrene)-graft-polystyrene(P(p-MS)-g-PS) copolymers. Khani et al. [40] investigated RAFT preparation of well-defined polyisoprene grafted silica nanoparticles (PIP-g-SiO₂NPs) while Bolton et al. [41] reported the synthesis of a poly(styrene)-b-poly(methyl methacrylate) (PS-PMMA) bottlebrush block copolymer with asymmetrical branches by RAFT and ATRP polymerizations. Hazer et al. [42] reported a range of polymers produced by RAFT polymerization of styrene (St), vinyl benzyl chloride (vbc), tertbutyl methacrylate (tert-BMA), and n-butyl methacrylate (nBMA) using carboxylic acid functionalized trithiocarbonate. Göktaş [43] synthesized poly(methyl methacrylate-b-styrene) and poly(methyl methacrylate-b-acrylamide) block copolymers in two steps via a redox polymerization method coupled with an atom transfer radical polymerization (ATRP) method. Lastly, Öztürk et al. [44] synthesized triarm block copolymers containing one polystyrene (or polyacrylamide) arm and two poly(β-butyrolactone) arms in one step by simultaneous use of RAFT polymerization of styrene (St) (or acrylamide, designated as AAm) and ROP of β-butyrolactone (BL) [45–48].

In this contribution, further utilization of RAFT polymerization is described utilizing brominated polyoleic acid (Pole-Br) synthesized by condensation polymerization. This Pole-Br was used as a suitable initiator for controlled/living radical polymerizations by acting as a novel macro RAFT agent in the exchange of the bromide groups of polyoleic acid with potassium ethyl xanthate resulting in poly(styrene)-*graft*-poly(oleic acid) graft copolymers. To our knowledge, PS-*g*-Pole graft copolymers will be brought to the literature with this study by combining RAFT and condensation polymerizations.

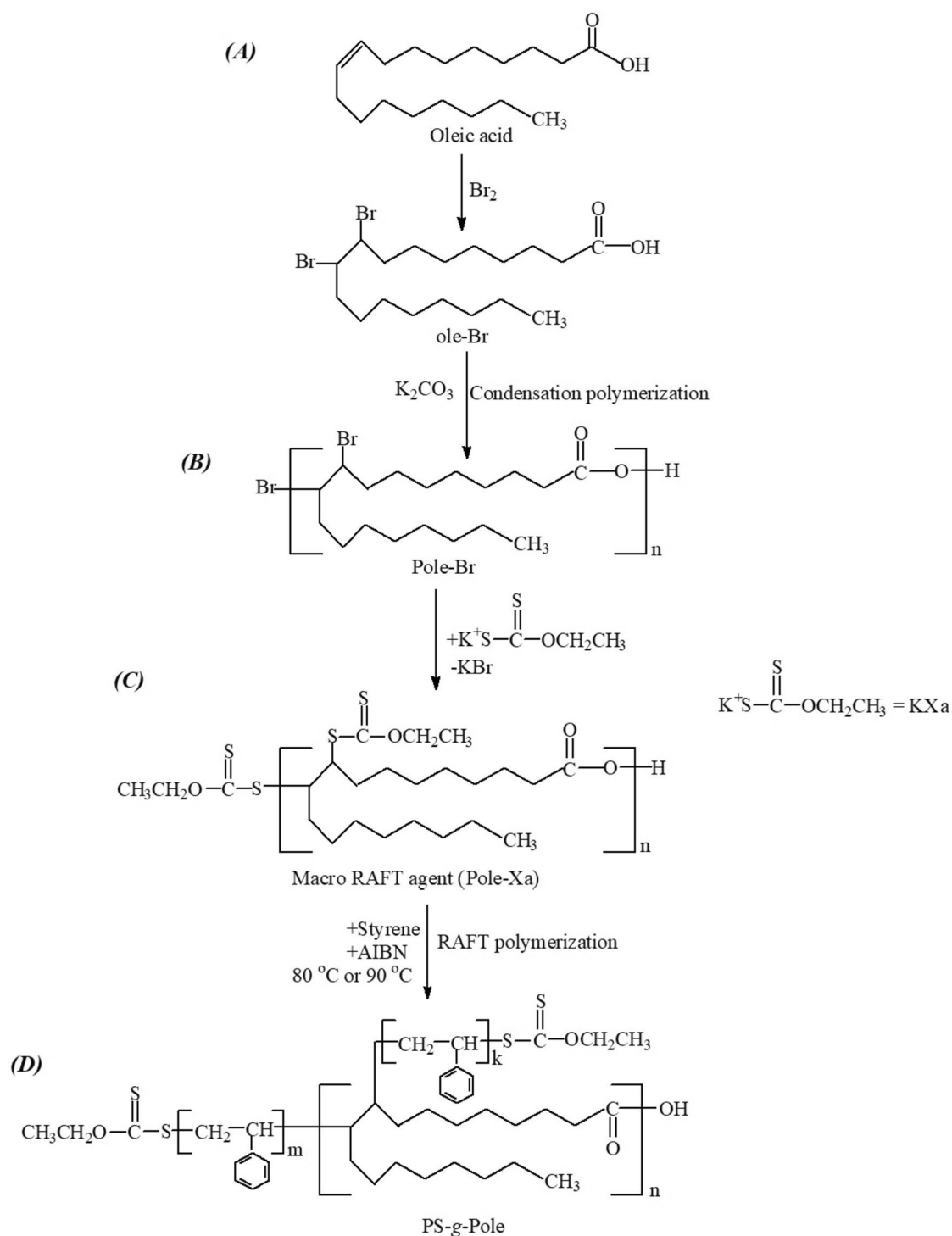
Experimental

Chemicals

Potassium ethyl xanthogenate salt (KXa), 2,2'-azobisisobutyronitrile (AIBN), oleic acid, styrene (S), tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) were supplied by Aldrich and used as received. Methanol, chloroform, petroleum ether, K₂CO₃, Br₂, and Na₂SO₄, were supplied by Fluka and used as received.

Synthesis of Polymeric Brominated Oleic Acid (Pole-Br) by Condensation Polymerization

2.7 g of Br₂, a 10 g solution of Br₂/CCl₄ (1:1) and 12 g of oleic acid solution [(CHS) oleic acid: 5.06 g/15 g CCl₄]



Scheme 1 The brominated oleic acid (ole-Br) (A), synthesis mechanism of Pole-Br (B), chemical synthesis reaction of macro RAFT agent (Pole-Xa) (C), Synthesis mechanism of PS-g-Pole graft copolymers (D)

were added into a glass flask and stirred in a water bath at room temperature for 24 h. The product was then poured into excess distilled water. The brominated oleic acid (ole-Br) was washed an additional two times with distilled water.

The oily phase was separated from the water phase and dried using anhydrous Na_2SO_4 . The yield for the obtained product was 7.18 g. The bromination of the oleic acid is shown in Scheme 1A. Referring to the condensation polymerization

mechanism, specified amounts of ole-Br, K_2CO_3 and DMF (Table 1) were added to a flask and stirred at 85 °C for 24 h resulting in polymeric brominated oleic acid (Pole-Br; Scheme 1B).

Synthesis of a Novel Oleic Acid-Based Macro RAFT Agent (Pole-Xa)

To synthesize the poly(oleic acid) macro RAFT agent (Pole-Xa), 1.12 g of polymeric brominated oleic acid (Pole-Br), 1.76 g of potassium ethyl xanthogenate (KXa) and 40 mL of THF were combined and mixed using a magnetic stirrer at room temperature for 72 h. The formed KBr and excess KXa salts were removed by filtration. The solvent was evaporated with a rotary evaporator and the product was washed with water, then with methanol and dried at room temperature for one week and subsequently under vacuum at 50 °C for 1 day. The chemical synthesis reaction of the macro-RAFT agent (Pole-Xa) is shown in Scheme 1C.

Synthesis of Copolymers by RAFT Polymerization

In accordance with the RAFT mechanism, various amounts of Styrene (S), 2,2'-azobisisobutyronitrile (AIBN) and RAFT agent (Pole-Xa) were placed in a Schlenk tube and allowed to form a homogeneous solution. The specific amounts of each chemical used in the polymerization reactions are given in detail in Table 2 and 3. Argon was passed through the solution. After closing the tube, polymerization was carried out in a silicone oil bath at 80 and 90 °C for between 1 and 5 h. At the end of the polymerization reaction, the contents of the tube were poured into excess petroleum ether and the poly(styrene)-*g*-poly(oleic acid) [(PS-*g*-Pole)] graft copolymer was precipitated and dried under vacuum for one week. The synthesis mechanism of PS-*g*-Pole graft copolymers is as shown in Scheme 1D.

Analysis

Molecular Weight Determination

The molecular weights and molecular weight distributions of the synthesized polymers were determined by gel-permeation chromatography (GPC) using a Malvern Viscotek GPCmax device with THF as the mobile phase. Each of the samples was weighed (~25 mg) and dissolved in 10 mL of THF. The dissolved samples were transferred to separate vials after passing each through a 0.22 PTFE syringe filter.

The conditions of each analysis were as follows: (1) Detector: VE 3580 RI detector, (2) TGuard + 2xT6000M column, (3) Solvent: THF, (4) Detector Temperature: 35 °C, (5) Column Temperature: 35 °C, (6) Injection volume: 100 μ L, (7) Flow rate: 1 mL/min, (8) Analysis time: 40 min/sample. A polystyrene (PS) calibration curve with 12 standards ranging from 1000 Da to 4.5 MDa was used for post-analysis calculations.

Composition Determination

Fourier transform infrared spectroscopy (FTIR) was utilized to determine the functional groups associated with the chemical intermediates (initiators) and final graft copolymers. The spectra were recorded with a Perkin Elmer (Shelton, CT USA) Spectrum 100 spectrometer in transmit mode with a scanning speed of 4000–550 cm^{-1} . Structural characterization of the synthesized initiators and the graft copolymers was performed by 1H -nuclear magnetic resonance (1H -NMR) spectroscopy on a Bruker Ultra Shield Plus, ultra-long retention time 400 MHz spectrometer using deuterated chloroform as solvent.

Thermal Property Determination

Thermal analyses of the synthesized polymers were performed using the Lab SYS EVO TGA/DSC thermo gravimetric analysis (TGA) device and differential scanning calorimetry (DSC) with the heating rate of 10 °C/min under Argon gas protection. The TGA temperature range was from 25 to 550 °C while DSC (calibrated with indium; $T_m = 156.6$ °C) was performed using a temperature range between 25 and 200 °C.

Results and Discussion

Synthesis of Polymeric Brominated Oleic Acid (Pole-Br) by Condensation Polymerization

In order to follow any chemical reaction it is imperative to properly analyze and understand the characteristics of the starting materials. In this study, oleic acid was utilized as the precursor for the synthesis of brominated oleic acid which was subsequently used in the formation of polymeric brominated oleic acid (Pole-Br) by condensation polymerization. The 1H -NMR scan of oleic acid (Fig. 1a) ascribes the protons associated with the terminal CH_3 group at 0.8 ppm,

Table 1 Conditions of condensation polymerization for the synthesis of Pole-Br

Code	Ole-Br (g)	K_2CO_3 (g)	DMF (g)	Yield (g)	Mn (g/mol)	Conv. (%)	M_w/M_n
POLE-Br	2.18	2.96	5.15	1.46	18,100	66.97	2.05

Table 2 Effectuate of polymerization time on the RAFT polymerization

Code	POLE-Xa (g)	Styrene (g)	AIBN (g)	Polym. time (min.)	Yield (g)	Conv. (%)	M _n GPC (g/mol)	M _w /M _n	M _n Theo (g/mol)	PS (wt%)	Pole (wt%)	Ln[Mo]/[M]	Decomp. temp. (°C)	
													T _{d1}	T _{d2}
PoleS-1	0.2013	5.0152	0.0055	60	0.7034	13.48	72,394	1.63	51,276	68	19	0.1480	160	420
PoleS-2	0.2055	5.0569	0.0055	120	1.3655	25.95	77,410	1.65	83,006	71	20	0.3034	180	420
PoleS-3	0.2049	5.0155	0.0055	180	1.6002	35.65	86,709	1.69	107,267	77	17	0.3812	180	420
PoleS-4	0.2063	5.0175	0.0055	240	1.8784	35.96	92,564	1.76	108,043	85	14	0.4655	180	420
PoleS-5	0.2060	5.0230	0.0055	300	2.2647	43.31	90,876	1.91	126,426	85	14	0.5948	170	420

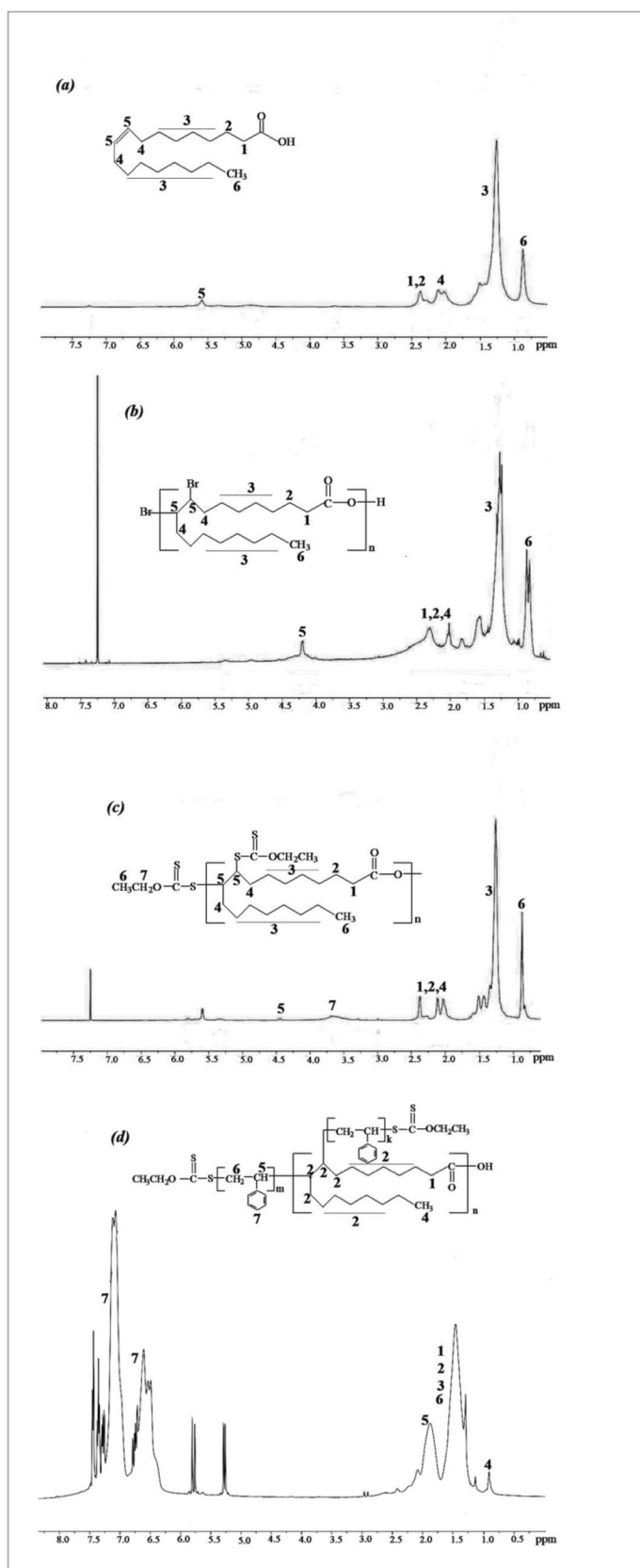
Polym. temp. = 80 °C

Table 3 Effectuate of polymerization time on the RAFT polymerization

Code	POLE-Xa (g)	Styrene (g)	AIBN (g)	Polym. time (min.)	Yield (g)	Conv. (%)	M _n GPC (g/mol)	M _w /M _n	M _n Theo (g/mol)	PS (wt%)	Pole (wt%)	Ln[Mo]/[M]	Decomp. temp. (°C)	
													T _{d1}	T _{d2}
PoleM-1	0.2038	5.0110	0.0055	60	1.4303	27.42	57,715	1.83	86,682	81	17	0.3338	160	420
PoleM-2	0.2021	5.0307	0.0055	120	1.7998	34.39	57,810	2.06	104,116	86	14	0.4366	170	420
PoleM-3	0.2004	5.0170	0.0055	180	1.8742	35.92	73,364	2.04	107,943	85	13	0.4643	170	420
PoleM-4	0.2050	5.0230	0.0055	240	2.2562	43.16	63,306	2.24	126,051	86	12	0.5917	170	420
PoleM-5	0.2006	5.0250	0.0055	300	2.0183	38.62	68,892	2.27	114,696	87	12	0.5085	180	420

Polym. temp. = 90 °C

Fig. 1 $^1\text{H-NMR}$ scans of oleic acid (**a**), Pole-Br (**b**), macro RAFT agent (Pole-Xa) (**c**), PS-g-Pole graft copolymer (**d**)



the protons associated with the internal CH_2 groups at 1.2 and 2.4 ppm, and the proton associated with the methine groups (CH) involved with the olefinic carbons at 5.6 ppm. Bromination and polymerization resulted in Pole-Br whose $^1\text{H-NMR}$ results are shown in Fig. 1b. By comparison, the resonance present at 5.6 ppm in the oleic acid result disappeared while a separate resonance at 4.2 ppm corresponding to CH-Br developed. This shift demonstrates the conversion of the olefinic groups in oleic acid to brominated carbons within the Pole-Br monomers. The FT-IR spectrum of the Pole-Br shows a C-Br band at 722 cm^{-1} , C=O band at 1720 cm^{-1} , an aliphatic CH band at 2920 cm^{-1} and an OH band at 3500 cm^{-1} which helped confirm the reaction (Fig. 2a). The molecular weight of the synthesized Pole-Br was 18,100 g/mol (number average molecular weight; M_n) with a polydispersity (\mathcal{D} ; M_w/M_n) of 2.05 (Table 1).

Synthesis of a Novel Oleic Acid-Based Macro RAFT Agent (Pole-Xa)

The Pole-Br (synthesis was described in “[Synthesis of Polymeric Brominated Oleic Acid \(Pole-Br\) by Condensation Polymerization](#)” Sect.), was subsequently used to produce the poly(oleic acid) macro RAFT agent (Pole-Xa) for use in the xanthate-mediated RAFT polymerization reaction. Successful synthesis of Pole-Xa was confirmed by $^1\text{H-NMR}$ (Fig. 1c) and FT-IR (Fig. 2b) of the final product. NMR resonances at 0.8 ppm (CH_3), 1.2 and 2.4 ppm (CH_2), 3.5 ppm (OCH_2), and 4.3 (CH-S) inferred the successful production of Pole-Xa. This result was further confirmed through FT-IR spectroscopy of the macro RAFT agent (Pole-Xa). Bands associated with the C=S group at 1600 cm^{-1} , the C=O group at 1720 cm^{-1} , an aliphatic CH group at $2852\text{--}2923\text{ cm}^{-1}$ and OH bands at 3500 cm^{-1} were present signifying the successful conversion of Pole-Br to Pole-Xa which was then used in the reaction to produce the poly(styrene-*graft*-oleic acid) copolymers (PS-*g*-Pole) through RAFT polymerization. The SEM and EDX analysis of macro RAFT agent (Pole-Xa) is given in Fig. 3. The molecular weight of Pole-Xa determined by GPC (M_n) was 18,400 g/mol.

Synthesis of the Poly(Styrene-Graft-Oleic Acid) Copolymers by RAFT Polymerization

RAFT polymerization of styrene (S) was performed at either 80 or 90 °C via a novel macro RAFT agent (Pole-Xa) obtained from the reaction of potassium ethyl xanthate (KXa) and Pole-Br resulting in poly(styrene-*graft*-oleic acid) copolymers (PS-*g*-Pole). For the first time in this study, PS-*g*-Pole graft copolymers were introduced to the macromolecular library with this RAFT polymerization in the presence of a polyoleic-based macro RAFT agent synthesized by condensation polymerization (described

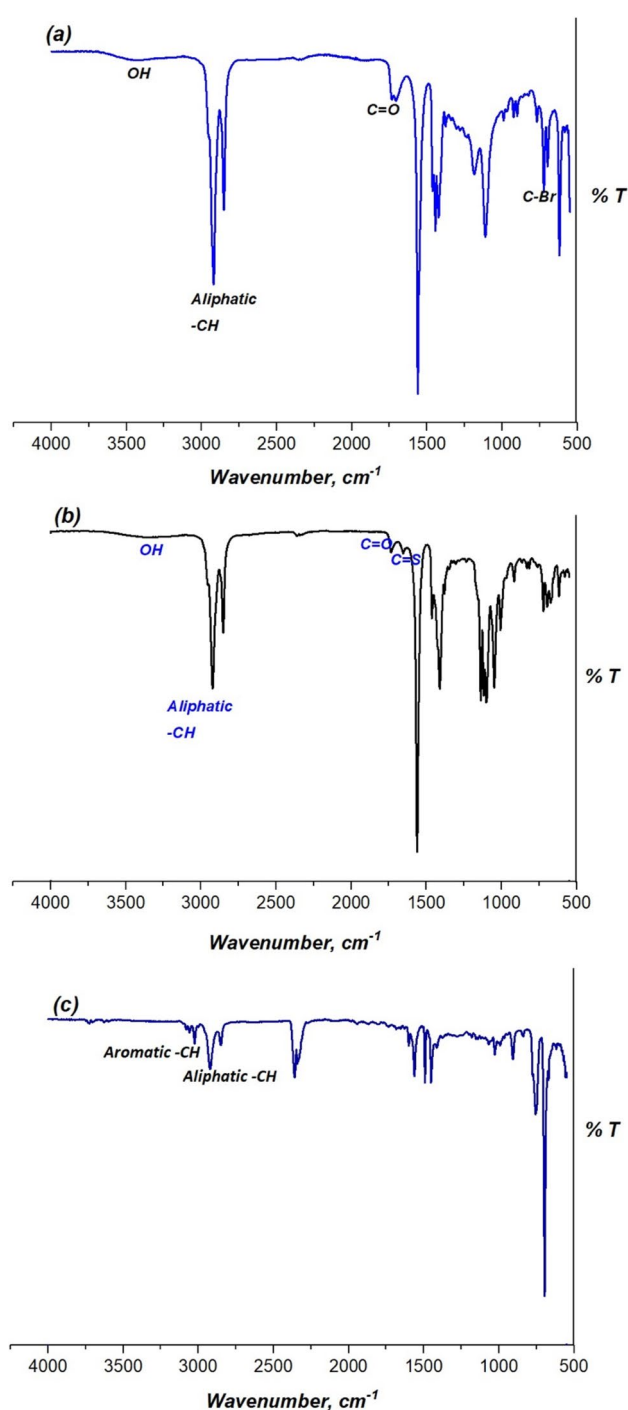
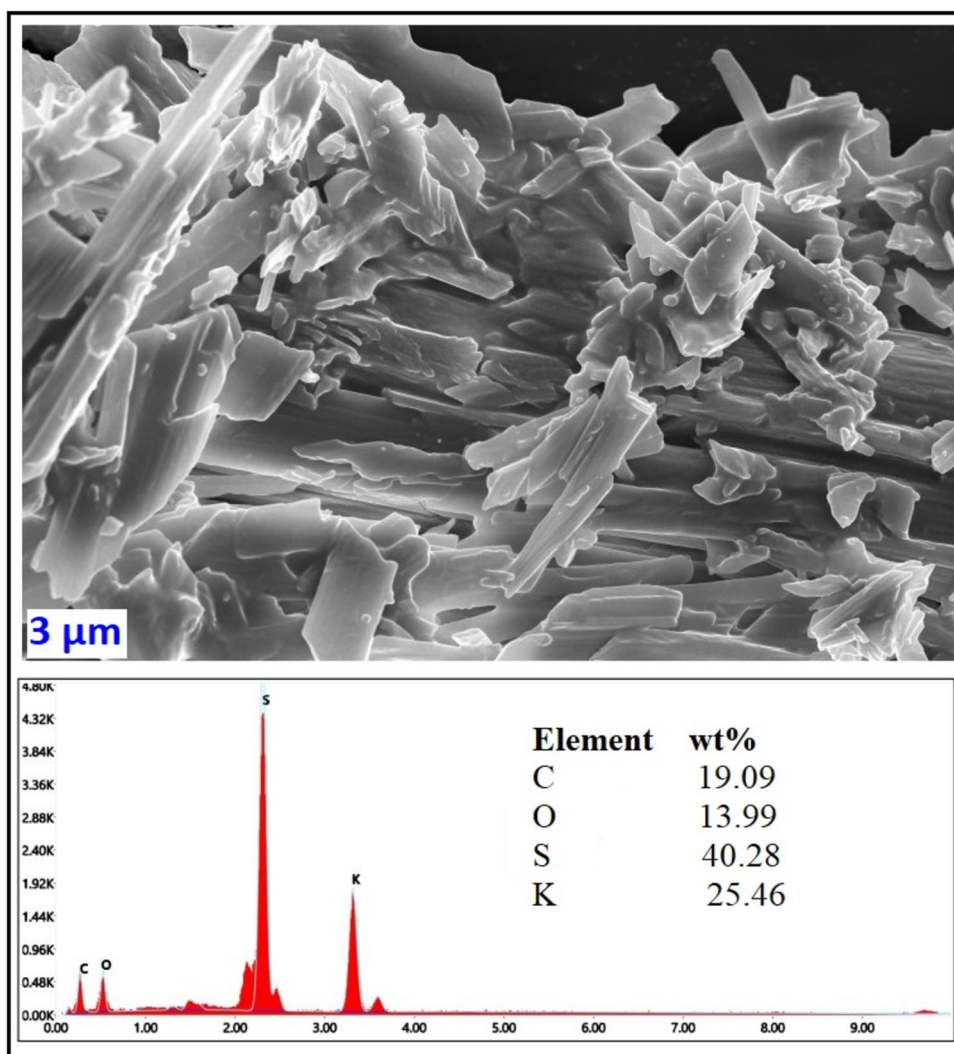


Fig. 2 FT-IR spectrum of Pole-Br (a), macro RAFT agent (Pole-Xa) (b), PS-*g*-Pole graft copolymer (c)

previously). The suitability of the Pole-Xa for use in the solvent-free xanthate-mediated RAFT polymerization of styrene was also reported for the first time with this paper. The $^1\text{H-NMR}$ of the PS-*g*-Pole graft copolymer show resonances at 0.9 ppm (CH_3), 1.2 ppm (CH_2) which correspond to the Pole block of the copolymer and the PS block of the

Fig. 3 SEM and EDX images of macro RAFT agent (Pole-Xa)



graft copolymers, and at 1.8 ppm (CH) which correspond to the PS block of the graft copolymers. Additionally, the protons associated with the phenyl groups were detected at between 6.6 and 7.2 ppm (Fig. 1d). In the FT-IR spectrum of the PS-g-Pole graft copolymer, bands corresponding to aliphatic CH ($2852\text{--}2923\text{ cm}^{-1}$) and aromatic CH (3025 cm^{-1}) were shown (Fig. 2c). The effects of polymerization time and temperature on polymer molecular weight and yield are shown in Table 2 and 3. Generally, the molecular weights of the synthesized PS-g-Pole graft copolymers were higher at identical polymerization times when produced at $80\text{ }^{\circ}\text{C}$ over those produced at $90\text{ }^{\circ}\text{C}$. However, as expected, at each temperature increased polymerization times resulted in larger molecular weights until a threshold polymerization time was reached where the molecular weights stabilized (Figs. 4 and 5). At $80\text{ }^{\circ}\text{C}$, as the polymerization times increased in 1-h increments, the M_n values of the graft copolymers increased by an average of $8.6 \pm 2.9\%$ per hour up to 4 h reaction time. Between 4 and 5 h the M_n stabilized and in fact, decreased

slightly by 1.8%. In contrast, at $90\text{ }^{\circ}\text{C}$ the M_n values of the graft copolymers were on average $23.4 \pm 6.0\%$ smaller than the graft copolymers produced at $80\text{ }^{\circ}\text{C}$ at the same polymerization times. In addition, the maximum M_n value for the graft copolymers produced at $90\text{ }^{\circ}\text{C}$ occurred at 3 h instead of 4 h (as at $80\text{ }^{\circ}\text{C}$) and the M_w/M_n for each of the graft copolymers produced at $90\text{ }^{\circ}\text{C}$ (with the exception of the polymers produced at 1-h), were above 2.00. By comparison, the M_w/M_n values of the polymers produced at $80\text{ }^{\circ}\text{C}$ were between 1.63 and 1.91. The reason why the M_w/M_n values were higher than expected is due to the high molecular weight of the initiator used in the polymerization and the presence of many active centers in the polymerization environment (Table 2 and 3). This phenomenon has been reported in our previous articles [18–20].

Conversion represents the amount of graft copolymer that was produced from a given amount of reactants. In this study at $80\text{ }^{\circ}\text{C}$ the yields (g) and conversion (%) increased from 0.70 to 2.26 g and from 13.48

Fig. 4 The effect of 80 °C polymerization temperature and polymerization time on molecular weight and conversion (Table 2)

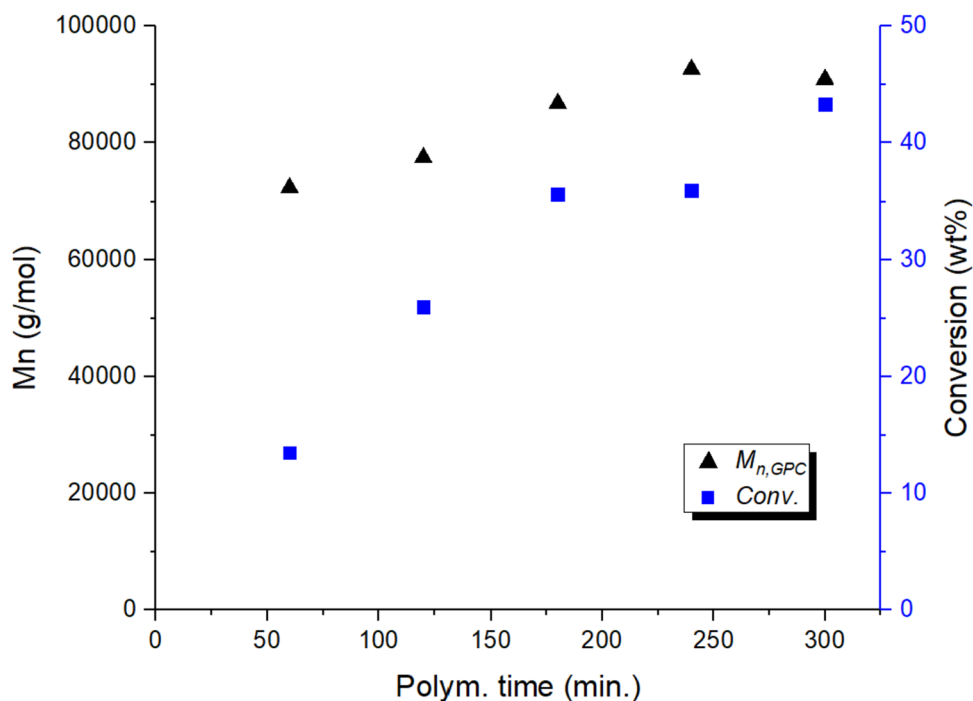
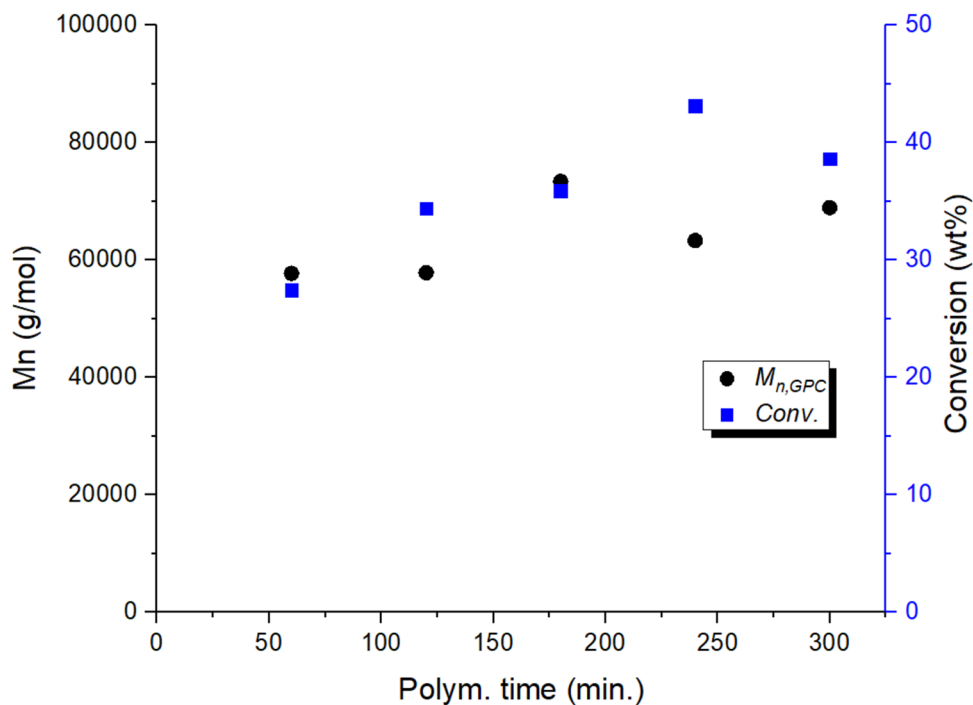


Fig. 5 The effect of 90 °C polymerization temperature and polymerization time on molecular weight and conversion (Table 3)



to 43.31% (Fig. 4; Table 2), respectively as the reaction times increased. At 90 °C the yield and conversion values were approximately 100% higher than those at 80 °C after 1 h reaction time but ultimately reached a comparative maximum (yield = 2.26 g; conversion = 43.16%) 1 h earlier than at 80 °C (Fig. 5; Table 3). This indicates that at 90 °C the reaction initiates quicker and terminates sooner but

ultimately, the maximum yields and conversions remained comparable.

Using the assumption that a RAFT agent compound forms a polymer chain in controlled/living radical polymerization methods, the theoretical molecular weight ($M_{n,theo}$) is calculated according to Eq. 1 [49]; where $[M]_0$ and $[RAFT-agent]_0$ are the initial concentrations of monomer and RAFT

agent, $(M_{\text{mon}})_0$ represents the molar weight of the monomer, and 18,400 represents the molar weight of the RAFT agent. The theoretical molecular weight ($M_{n,\text{theo}}$) calculated according to Eq. 1 is shown in Tables 2 and 3.

$$M_{n,\text{theo}} = 18400 + \{([M]_0 / [\text{RAFT agent}]_0)\} \times \text{conversion} \times M_{\text{mon}} \quad (1)$$

The weight percentages of each block in the structure of the graft copolymers were also determined by calculating the peak areas of methyl protons in Pole (0.8 ppm) and phenyl protons in polystyrene (6.6–7.2 ppm) in $^1\text{H-NMR}$. In PS-*g*-Pole graft copolymers, PS was calculated in the range of 68–87% and Pole was calculated in the range of 12–20%. It can be said that the increase in both polymerization time and polymerization temperature (90 °C) increases PS % and Pole % (Tables 2 and 3).

Investigation of Polymerization Kinetics

It is known that controlled/living polymerization systems occur according to first-order reaction kinetics. The kinetics of the first order reactions are calculated according to the following equation.

$$\ln \frac{[M_0]}{[M]} = kt$$

where $[M_0]$ and $[M]$ values represent the monomer concentrations at the beginning and at the end of the polymerization reaction at specific times, respectively. The t term is the polymerization time. The term “ k ”, which is used with concentrations in writing reaction rate relations, is the rate constant of the reaction. The reaction rate constant shows the effect of temperature on the reaction rate and varies from reaction to reaction. Changing the temperature at which the reaction takes place can significantly affect the value of “ k ”.

In this study, the polymerization was performed at two different temperatures (80 and 90 °C). The effect of temperature on polymerization kinetics was investigated. From the linear parts of the graph $\ln [M_0]/[M]$ and t , the rate constant k was calculated for both temperatures and are shown in Figs. 6 and 7, respectively. The rate constant “ k ” changed significantly with changing the polymerization temperature. Specifically, the rate constants were found to be 1.83×10^{-3} L/mol/dk for the 80 °C reaction and 7.27×10^{-4} L/mol/dk for the 90 °C reaction.

Investigation of Thermal Properties of Graft Copolymers

The thermal properties of the graft copolymers synthesized at both 80 and 90 °C were investigated by thermogravimetric analysis (TGA), and differential scanning calorimetry

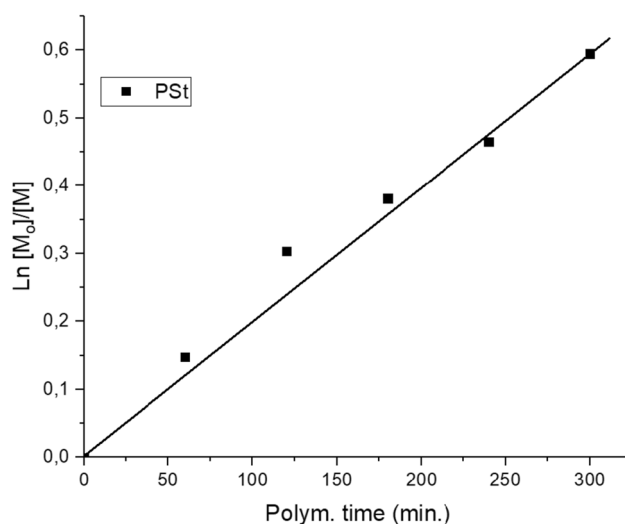


Fig. 6 Time dependence of $\ln (M_0/M)$ for RAFT polymerization at 80 °C

(DSC). TGA analysis of the graft copolymers revealed two decomposition temperatures. It was observed that the weight loss and decomposition temperatures (T_d) of the graft copolymer were at 160 °C corresponding to the Pole and 420 °C corresponding to the PS segments, respectively (Figs. 8 and 9). The thermal transition temperatures of the PS-*g*-Pole graft copolymers were determined by DSC analysis. A glass transition temperature (T_g) was observed around 60–65 °C for both of the graft copolymers (Fig. 10) with no indication of a melting endotherm. These results suggested that the graft copolymers were either amorphous with limited to no crystallinity or exhibited isodimorphic behavior between the two chain segments of the graft copolymer. Additionally, these results may also be explained by the reduction of homopolymer formation and the high rate of graft copolymer formation.

Conclusions

In this study, Poly(styrene-*graft*-oleic acid) graft copolymers with different Pole and PS block lengths were successfully prepared by combining condensation polymerization followed by RAFT polymerization as evidenced by FT-IR, $^1\text{H-NMR}$, GPC, TGA, DSC and SEM-EDX analysis. In general, the molecular weights of the synthesized graft copolymers were higher when produced at 80 °C than those produced at 90 °C at the same polymerization times. However, as expected, increasing polymerization times at each temperature resulted in larger molecular weights until a threshold polymerization time was reached at which the molecular weights stabilized. The rate constant “ k ” changed significantly with changing the polymerization temperature.

Fig. 7 Time dependence of $\ln(M_0/M)$ for RAFT polymerization at 90 °C

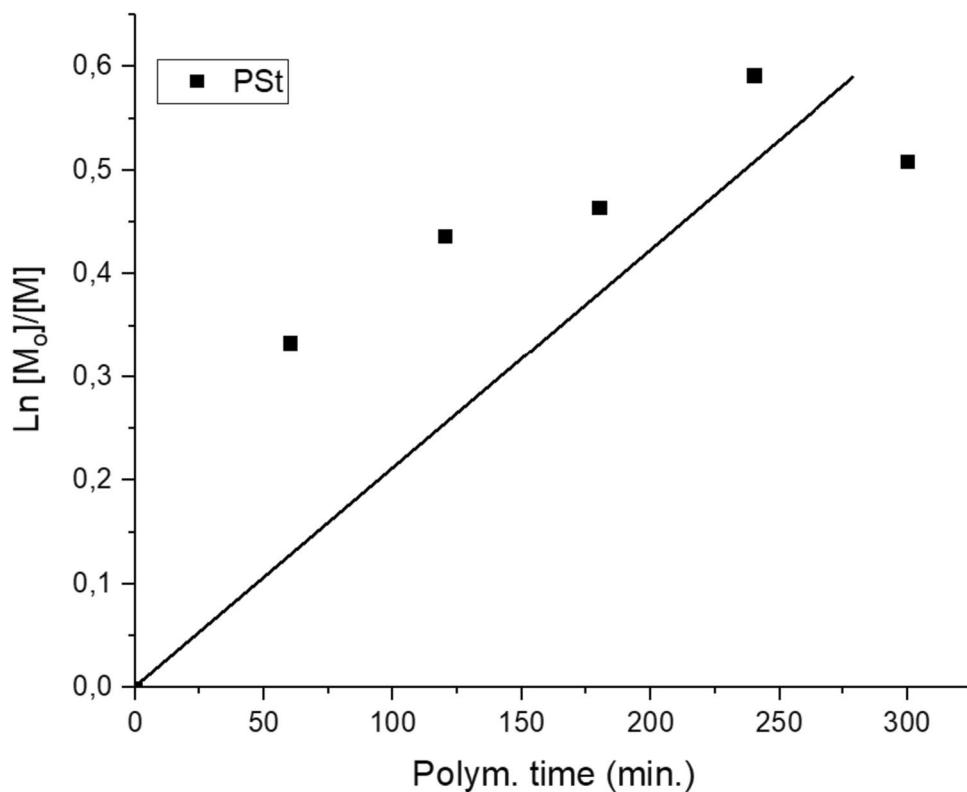


Fig. 8 TGA mass loss curves of PS-g-Pole graft copolymer (PoleM series in Table 3)

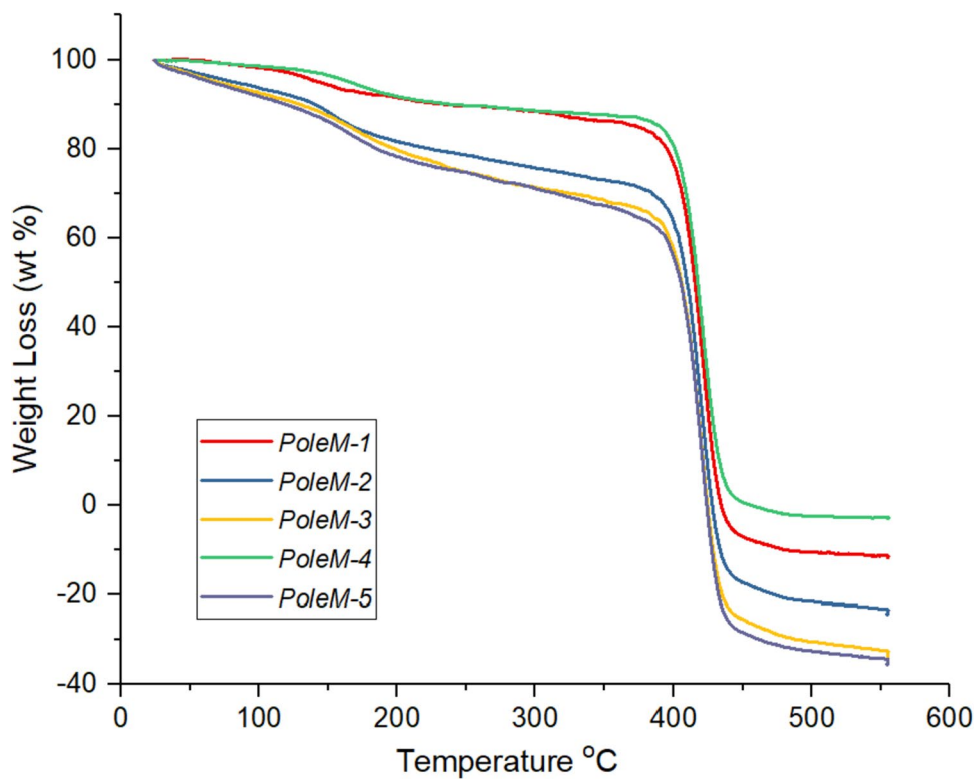


Fig. 9 dTG curves of PS-*g*-Pole graft copolymer (PoleM series in Table 3)

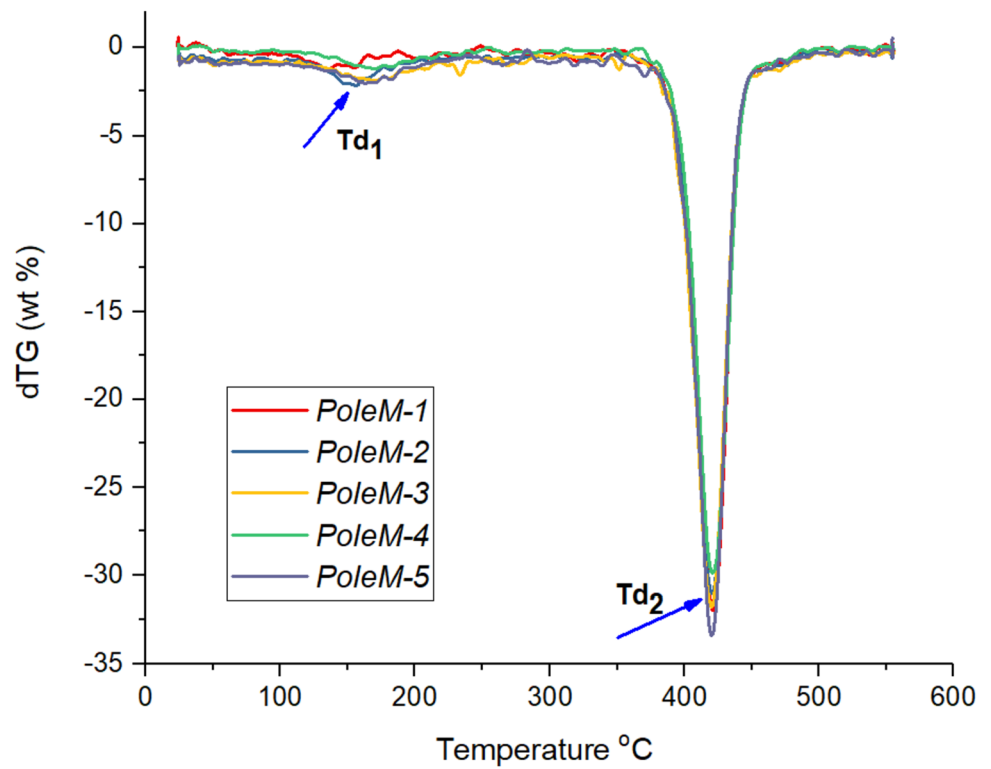
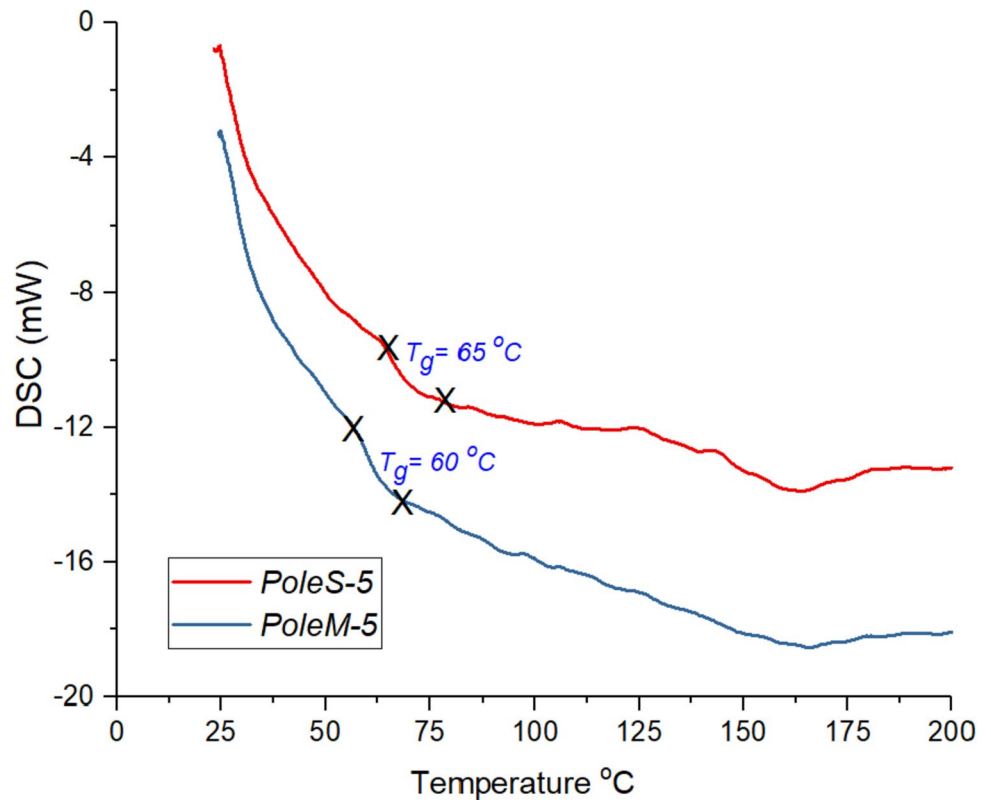


Fig. 10 DSC curves of PS-*g*-Pole graft copolymer (PoleS-5 in Table 2 and PoleM-5 in Table 3)



Specifically, the rate constants were found to be 1.83×10^{-3} L/mol/dk for the 80 °C reaction and 7.27×10^{-4} L/mol/dk for the 90 °C reaction. A glass transition temperature (T_g) of around 60–65 °C was observed for the graft copolymers synthesized at both 80 and 90 °C and no signs of melting endotherms were observed. These results showed that the graft copolymers were either amorphous and had limited or no crystallinity or exhibited isodimorphic behavior between the two types of chain segments. It can be explained by the good mixing of Pole and PS homopolymers with RAFT polymerization by recording a glass transition temperature (T_g) for graft copolymers. Observation of two different degradation temperatures by TGA analysis may also confirm the formation of bi-block graft copolymer. It can be said that RAFT polymerization at two different temperatures affects the molecular weight of the graft copolymer as well as the polymerization kinetics and accordingly the "k" rate constant. In this contribution, it could be determined that the graft copolymer production by using RAFT and condensation polymerization have superior properties to other traditional polymerization techniques, and examining the kinetic properties of graft copolymers may also contribute to polymer science.

Author contributions MG: Supervision, Conceptualization; CA: Conceptualization; BH: Supervision, Conceptualization. RA: Conceptualization.

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Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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