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ORIGINAL RESEARCH

Synthesis and characterization of polyvinyl alcohol-g-polystyrene copolymers via MADIX polymerization technique

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Abstract

In polymer structure design, branching can occur randomly or by reactions designed to target specific architectures. This microstructural property affects many physical properties such as polydispersity, molecular weight and polymer chain size. A new reversible addition-fragmentation chain transfer/macromolecular design through interchange of xanthates (RAFT/MADIX) agents with polyvinyl alcohol was performed. In the process, polyvinyl alcohol (PVA), potassium hydroxide, carbon disulfide and derivatives of benzoylchloride were employed, and thus, three new graft chain transfer agents (g-CTA) were synthesized. PVA-g-PS graft copolymers were obtained using MADIX agents by changing various factors including initiator, amount of monomer and reaction time. While the linear increase in molecular weight with monomer consumption was observed, the polymerization reaction was kinetically detected to be the first order. Significant progress has been made in controlling the molecular weight distribution of the polymer by RAFT polymerization. The synthesized graft copolymers were characterized using FTIR, ^{1}H NMR, ^{13}C NMR, GPC and DSC techniques. Also, the three new graft chain transfer agents were characterized by elemental analysis and the existence of xanthate -S-(C = S) O-PVA was confirmed. The synthesis of the copolymer with the MADIX agent, which has an almost infinite number of design possibilities, was successfully achieved. As a result, well-defined statistical PVA-g-PS copolymers having a narrow molecular weight distribution (PDI 1.23–1.47) were obtained.

Keywords MADIX/RAFT agent · Graft copolymer · Polyvinyl alcohol · Xanthate · g-CTA

Introduction

Polyvinyl alcohol (PVA) is used in many fields such as biotechnology [1, 2], hydrogel [3, 4], drug distribution [5], and biosensor and biomedical applications [6, 7] due to its promising properties. Enriching polyvinyl alcohol with copolymer groups converted into different polymers increases its application [8, 9]. The new design architectures of graft and block copolymers [10] enriched with copolymer groups have attracted great attention in many fields. As it is known, graft polymers have various structures, molecular weights, and functionality. Therefore, they exhibit high performance and controllable polymer material properties [11, 12]. The controllability of polymer materials is made possible by controlled radical polymerization. Until now, many studies have been done on controlled radical polymerization, including ATRP [13, 14], NMP [15], and RAFT [16, 17]. Since its initial discovery, the RAFT polymerization technique [18] has attracted great attention due to its unique advantages, stability, and popularity compared to live polymerization techniques. The macromolecular design (controlled/living free-radical polymerization (C/LRP) systems) by the modification of RAFT and xanthates (MADIX) has been extensively studied. The advantage of RAFT/MADIX polymerization technique is that the synthesized effective chain transfer agent can be selected depending on the functional groups [19–21]. In terms of reaction control, the MADIX and RAFT processes are different due to the nature of chain transfer agent (CTA) [22, 23]. An example of MADIX agent synthesis is poly(ethylene glycol) xanthate synthesized by macro-RAFT agents, which is successfully used in the controlled polymerization of styrene [24]. Controlled synthesis of graft and block copolymer RAFT polymerization

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technique was successfully carried out. According to the literature, similar studies have been done in the synthesis of polyvinyl alcohol using the RAFT technique [25, 26]. Ma'Radzi et al. designed PVA stereoblock copolymer with living cationic vinyl polymerization and RAFT/MADIX polymerization [8]. Mishra et al. performed the sequential synthesis of the well-defined (PVAc-*b*-PS) and (PVA-*b*-PS) copolymers by the RAFT technique [27].

In our present study, it was aimed to synthesize a graft copolymer consisting of polyvinyl alcohol and polystyrene utilizing g-CTA. The copolymer synthesis with MADIX agent was successfully achieved. Well-defined statistical PVA-g-PS copolymers with a narrow molecular weight distribution were obtained (PDI 1.23–1.47). Whereby the narrow molecular weight distribution and structural control (molecular weight and other parameters such as branching) of the synthesized macrograft polymer, the product range and its practicality were improved.

Experimental

Materials

All chemicals used in the experiments were analytical grade and used without any further purification. For cleaning glassware, deionized water was used. Polyvinyl alcohol (PVA, $M_W \backsim 6000$, and 78% hydrolyzed) was purchased from Across Organics (Belgium). Potassium hydroxide (KOH 85%), benzoyl chloride (C_6H_5COCl 99%), *p*-tosyl chloride (C_7H_8COCl 98%), 4-chloro benzoylchloride ($C_6H_5COCl_2$ 99%), styrene (St) and 2,2'-azobisisobutyronitrile (AIBN, 99%) were purchased from Sigma-Aldrich (USA). Carbon disulfide (CS_2 99%) and diethyl ether ($C_4H_{10}O$ 99.5%) were obtained from Merck (Germany). Petroleum ether (99%), sodium carbonate (99.5%), dimethyl sulfoxide (DMSO 99%) and methanol (CH_3OH 99%) were purchased from Sigma-Aldrich (USA).

Instrumentation

Gel permeation chromatography (GPC) was used to determine the molecular weight (M_n) as well as polydispersity index (PDI). GPC chromatograms were obtained using a Waters 510 instrument using THF as the solvent for a flow rate of 1 mL/min, and with a Waters 1515 isocratic HPLC pump equipped by a Waters 2414 refractive index detector and three Waters Styragel HR columns. A calibration curve generated with six 13,000, 25,000, 50,500 72,000, and 96,400 Da for low dispersity was purchased from Polyscience. FTIR spectra were used to record the polymer films cast from $CHCl_3$ solutions, using a Bruker Alpha-P spectrometer. ^{1}H NMR BrukerAvance III HD 600 MHz model (Germany) was used for the characterization of the structure of organic compounds. ^{13}C NMR BrukerAvance III HD 150 MHz model was used to identify organic compounds. DSC analyses were performed by a Shimadzu 60 differential scanning calorimeter (Japan) in a nitrogen atmosphere at a flow rate of 10 mL/min. A BUCHI R-200 model evaporator (Germany) was used to evaporate the solvent from solutions. An LECO CHNS-932 Elementary Chemical Analyzer (USA) was used to determine C, H, N, and S element percentages with high precision by incineration of substances weighed 1–10 mg.

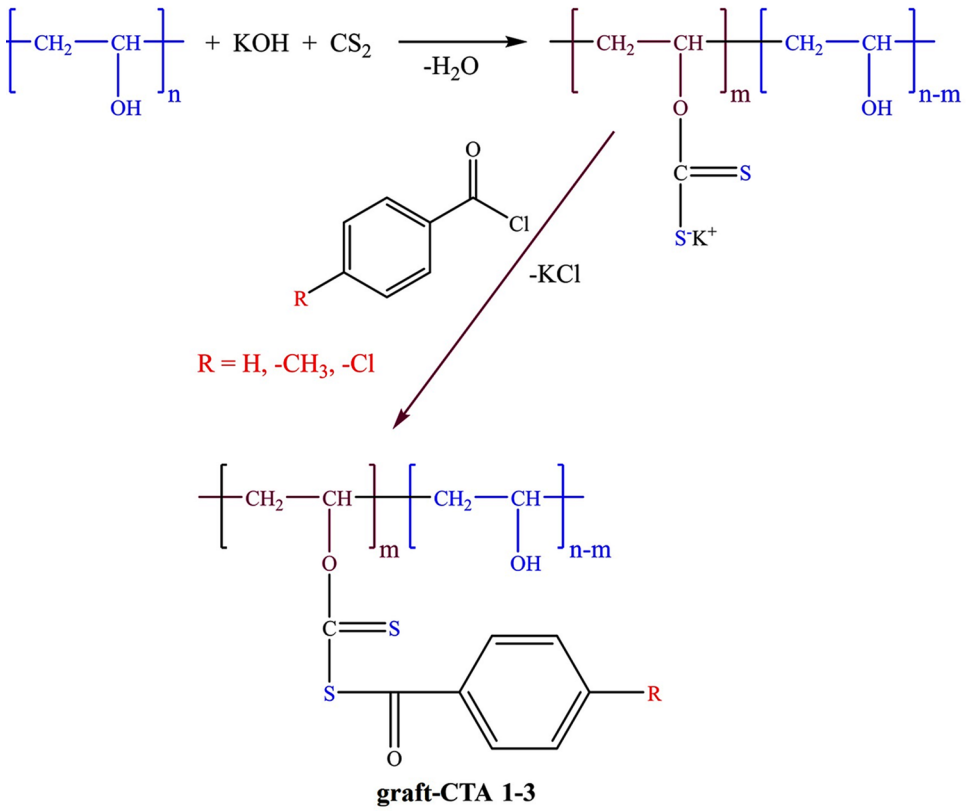
PVA-6000 benzoyl xanthate macro-MADIX agent synthesis-*g*-CTA 1

A solution including 5 g (8.33×10^{-4} mol) of PVA-6000 and 25 mL of DMSO was mixed in a flask, and the mixture was stirred until the PVA-6000 was dissolved. KOH (3.73 g, 0.066 mol) was added to the resulting solution and stirred until a yellow color was observed at 0 °C. The system was cooled to room temperature and 4 mL (0.066 mol) of CS_2 was slowly transferred onto the solution and stirring continued until the 2nd color cycle was observed (color changed from yellow to orange). The xanthate salt was obtained by adding potassium hydroxide and carbon disulfide to PVA. The g-CTA's 1–3 were synthesized with xanthate salt in the presence of benzchloyl chloride. The reaction was stopped when the 3rd color turn (straw yellow) was observed. The mixture was filtered. The solvent was evaporated in vacuo. The macro g-CTA was precipitated in a mixture of 50 mL of 1:1 diethyl ether:petroleum ether and allowed to stand for 24 h (Scheme 1). The g-CTA was dried in a vacuum oven. As a result of the reaction, the product was found to be 4.11 g and the yield was 82.3%. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: (5H, COC_6H_5), 7.97, 7.96, 7.63, 7.58, 7.50 (CH-O–H) 4,62 (Alf-H) 4.90, 4.56, 3.84, 2.53, 1.32 ppm. ^{13}C-NMR (100 MHz $CDCl_3$,25 °C)δ_C: (all OCH) 39.83, 40.63, (all CH_2) 42.95, (Ar-C4) 128.71, (Ar-C3) 130.60, (Ar-C2) 134.14, (-C(=S)-S) 163.15 ppm. FTIR spectrum (υ, cm^{-1}): 3067–2550 (-CH=C-H), 1678–1579 (-C=O), 1322–1286 (-C=S).

Copolymerization of styrene with PVA-6000 benzoyl xanthate macro-MADIX agent

Initial molar ratio of each component was [St]/[*g*-CTA1]/[AIBN] = 1000:9.4:1.6. DMSO. (15 mL) was added into 10 mL (0.0874 mol) styrene. An amount of 0.02 g (1.39×10^{-4} mol) of AIBN was added to this mixture and stirred until a homogenous solution was formed. After forming the solution, 0.151 g (8.211×10^{-6} mol) of g-CTA 1 was added. Ten samples were placed in an ultrasonic bath for 10 min, and then, argon gas was passed through the medium

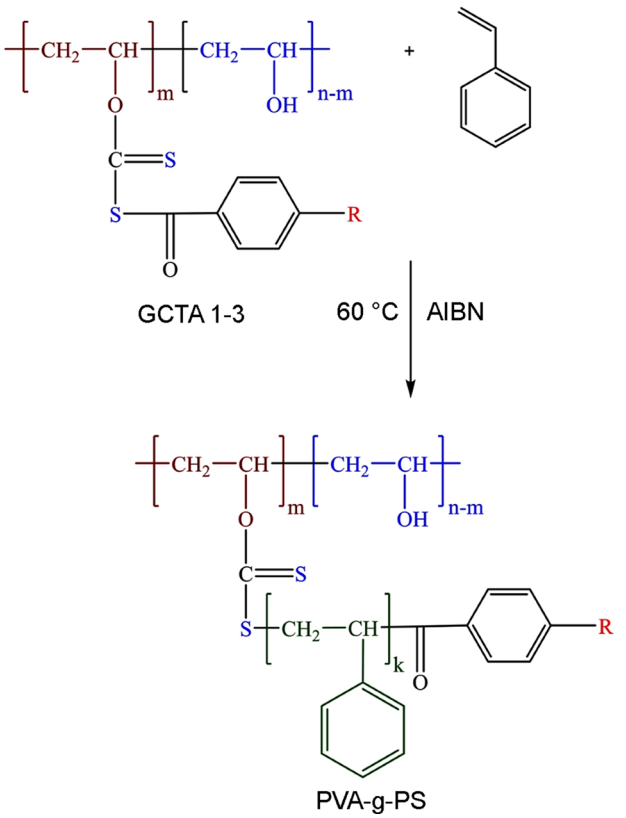
Scheme 1. Polyvinyl alcohol xanthate macro-RAFT agent synthesis



to obtain an inert atmosphere. Polymerization was started at 60 °C. Poly (PVA-*g*-ST) graft copolymers were precipitated by pouring into methanol at periodic intervals of 24 h. The graft copolymers were dried in a vacuum oven at 45 °C at 200 bar pressure. The reaction steps are shown in Scheme 2. ^{1}H NMR (400 MHz, ppm) δ 7.95 (d, J = 7.9 Hz, 1H), 7.52 (q, J = 9.4, 7.7 Hz, 1H), 7.33 (s, 1H), 7.11 (s, 7H), 6.58 (s, 2H), 3.78 (s, 2H), 3.33 (s, 8H), 2.50 (s, 27H), 2.46 (s, 1H), 1.80 (s, 2H), 1.34 (s, 6H). FTIR spectrum (υ, cm^{-1}): 3080–2848 (-CH = C-H), 1716–1620 (-C = O), 1180–1026 (-C = S).

PVA-6000 *p*-tolyl xanthate macro-MADIX agent synthesis-*g*-CTA 2

A similar procedure given above was conducted to prepare PVA-6000 *p*-tolylxanthate macro-MADIX agent synthesis-g-CTA 2. For this purpose, another mixture containing 8.9 mL (0.066 mol) of *p*-tollyl chloride was prepared and stirred for a while. The solid sample in the mixture was filtered. As a result of the reaction, the product was found to be 2.51 g and the yield was 50.34%. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: (5H, COC_6H_5) 7,99, 7.62, 7.48, (Ar-CH_3) 7.03, (CH-O–H) 4,32, (Alf-H) 4.20, 4.07, 3.84, 2.63, 1.22 ppm. ^{13}C-NMR (100 MHz $CDCl_3$,25 °C)δ_C: (all OCH) 39.43, 40.35, (all CH2) 41.95, (Ar-C4) 127.71, (Ar-C3)130.60, (Ar-C2) 132.14, (-C(= S)-S) 166.15 ppm. FTIR



Scheme 2. Synthesis of poly(PVA-g-ST) graft copolymers

spectrum (υ, cm^{-1}): 3048–2339 (-CH = C-H), 1809–1514 (-C = O),1019–942 (-C = S).

Copolymerization of styrene with PVA-6000 *p*-tolyl xanthate macro-MADIX agent

Initial molar ratio of each component was [St]/[*g*-CTA2]/[AIBN] = 1000:9.3:1.6. DMSO (15 mL) was added over 10 mL (0.0874 mol) of styrene. AIBN (0.02 g, 1.39×10^{-4} mol) was added and stirred until dissolved. *g*-CTA 2 (0.1594 g, 8.133×10^{-6} mol) was added. ^{1}H NMR (400 MHz, ppm) δ 7.55 (s, 1H), 7.13 (s, 2H), 3.83 (s, 1H), 3.32 (d, J = 9.5 Hz, 2H), 2.50 (s, 8H), 2.46 (s, 1H), 1.75 (s, 2H), 1.34 (s, 1H). FTIR spectrum (υ, cm^{-1}): 3129–2848 (-CH = C-H), 1600–1368(-C = O), 1200–1026 (-C = S).

PVA-6000 4-chloro benzoyl xanthate macro-MADIX synthesis agent -*g*-CTA 3

To synthesize PVA-6000 4-chloro benzoyl xanthate macro-MADIX synthesis agent -*g*-CTA 3, a mixture of 8.55 mL (0.066 mol) of 4-chloro benzoyl chloride was achieved and stirred for 15 min. The resulting mixture was filtered. As a result of the reaction, the product was found to be 4.87 g and the yield was 97.53%. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: (5H, COC_6H_5) 8,03 7.68, 7.37, (CH-O–H) 4,41, (Alf-H) 4.21, 4.11, 3.75, 2.43, 1.42 ppm. ^{13}C-NMR (100 MHz $CDCl_3$,25 °C)δ_C: (all OCH) 38.43, 40.55, (all CH_2) 40.95, ($OCHCH_2$) 80.42, (Ar-C4) 128.71, (Ar-C3)129.60, (Ar-C2) 131.14, (Ar-C1) 132.32, (C (= S) S) 165.05 ppm. FTIR spectrum (υ, cm^{-1}): 3093–2364 (-CH = C-H), 1796–1588 (-C = O), 1237–1110 (-C = S), 923–849 (-C–Cl).

Polymerization of PVA-6000 4-chloro benzoyl xanthate macro-MADIX agent with styrene

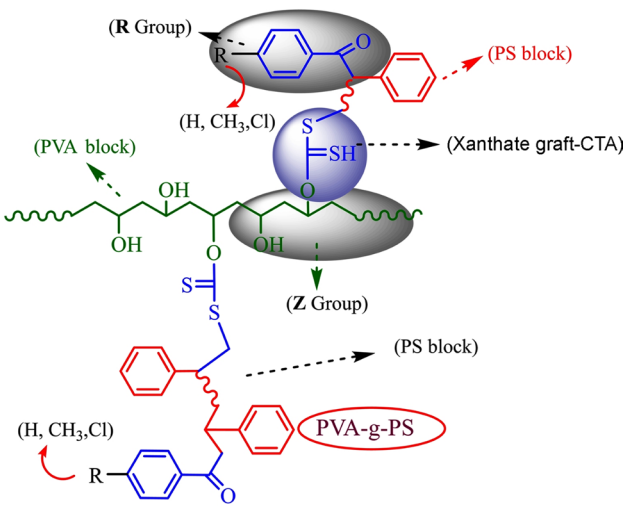
Initial molar ratio of each component was [St]/[*g*-CTA3]/AIBN] = 1000:9.7: 1.6. DMSO (15 mL) was added over 10 mL (0.0874 mol) of styrene. AIBN (0.02 g, 1.39×10^{-4} mol) was added and stirred until dissolved. *g*-CTA 3 (0.1775 g, 8.404×10^{-6} mol) was added. ^{1}H NMR (400 MHz, ppm) δ 7.09 (s, 2H), 6.56 (s, 1H), 3.33 (s, 2H), 2.50 (s, 8H), 1.78 (s, 2H). FTIR spectrum (υ, cm^{-1}): 3081–2849 (-CH = C-H), 1734–1366 (-C = O), 1067–1026 (-C = S), 842–754 (-C–Cl).

Results and discussion

MADIX agent was prepared and used in a controlled polymerization of styrene to produce well-defined statistical graft copolymers. Polyvinyl alcohol and polystyrene [28] are important commercial polymers. Here, graft copolymer synthesis is targeted. However, graft copolymers cannot be prepared easily such as other controlled methods [27]. Therefore, the graft polymerization of polyvinyl alcohol-*g*-polystyrene was carried out in a controlled manner by a specific macro-g-CTA prepared from polyvinyl alcohol.

MADIX polymerization is based on the radical activity of xanthate groups at the ends of the macromolecule chain. A suitable design of xanthate RS-(C = S) OZ used as a reversible transfer agent is essential for optimal control of molar masses and PDIs in the resulting polymer [29, 30]. There are two approaches to design an RAFT agent: R and Z group design which activates to -C (= S) -S binding in degenerative chain transfer [29]. In our study, the reaction for the synthesis of the graft copolymer was initiated to form RAFT agent units on polyvinyl alcohol. Most of the -OH groups on PVA have been converted to RAFT agent. This situation can be seen in IR shown in Fig. S1, S2 andS3. In the macro-g-CTA, while the PVA chain was used as a Z group, benzoyl chloride and derivatives were used as R groups. It was determined to be effective in degenerative chain transfer of structures selected as the R group which was responsible for repolymerization [20, 31]. Graft copolymers were obtained with a good PDI in the range of 1.23–1.47. The schematic diagram for the formation of PVA-g-PS is shown in Scheme 3. RAFT agents were obtained by reaction with PVA, CS_2 and aromatic acyl chlorides. Macro g-CTA agents were characterized by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. OriginPro 2018 program was used to visualize all the data obtained.

The elemental analysis has been applied to determine the sulfur binding percentages of MADIX/RAFT agents with high accuracy [32]. Elemental analysis and theoretically calculated values of carbon (C)%, hydrogen (H) % and sulfur (S) % ratios in the macro-RAFT agents are given in Table 1 and Fig. 1. The



Scheme 3. Proposed diagram for formation of PVA-g-PS graft copolymer

Table 1 Elemental analysis results of PVA-based benzoyl chloride derivative xanthate macro-g-CTA1-3

g-CTA's code	[a]Theo % (C)	[b]Exp % (C)	Theo. % (H)	Exp % (H)	Theo % (S)	Exp % (S)	[a] % S rate in structure
[c]PVB-6000	53.68	56.36	4.23	6.394	25.11	5.584	22.24
[d]PVP-6000	55.34	51.04	4.87	7.191	23.80	4.151	17.44
[e]PVK-6000	47.23	51.27	3.48	4.401	22.09	4.538	20.54

[a]Calculated stoichiometrically

[b]From the elemental analyzer

[c]PVB- chloride series

[d]PVP-4-methylbenzoyl chloride series

[e]PVK-4-chlorobenzoyl chloride series

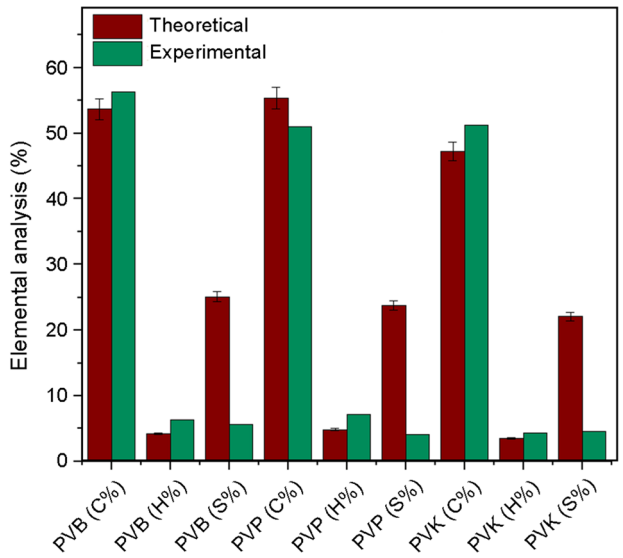


Fig. 1 Elemental analysis of macro-g-CTAs

amount of C, H, and S in the compounds, g-CTA's % S ratios PVB, PVP, and PVK were found to be 22.24, 17.44, and 20.54, in the stated order. These results confirmed the formation of sulfuryl groups in the g-CTA structure. It can be evaluated that the –OH groups on polyvinyl alcohol can form 80% macro g-CTA. The –C (=S) –S/OH ratio was found to be around 0.2 in the synthesized agents.

The rapid equilibrium formation in xanthate chain transfer polymerization enables a closer value of theoretical and experimental molar mass [33]. Ideally, as with other controlled polymerizations, molar masses increase linearly with the consumption of monomers by the effect of the chain transfer agent, and it can be predicted by Eq. 1:

$$\overline{Mn},\text{theo} = \frac{[M]_o}{f[M]\text{g} - \text{CTA}} \times M\text{MW} \times Conv. + M\text{g} - \text{CTA}, \quad (1)$$

where $\overline{Mn}$, theo is the theoretical number-average molar mass, $[\text{M}]_o$ is the initial monomer concentration, $[M]\text{g} - \text{CTA}$ is a concentration of g-CTA, f is the initiator efficiency, and MMW and $M\text{g} - \text{CTA}$ are the molar masses of the monomer unit and the xanthate g-CTA, respectively. The *Conv.* is the fractional conversion of the monomer.

The success of radical polymerizations is based on initiator efficiency [34]. Radicals formed by thermal decomposition, light, or other initiators initiate polymerization [35]. The number of initiators also indicates the number of formed chains. The degree of polymerization is used to determine the number of monomers per chain. However, in the polymerization process, theoretical and experimental data are generally incompatible [35]. This is since each radical formed in the starting step is linked to the formation of the active polymer chain.

The free-radical species undergo a lattice effect due to the solvents and monomers around them, in which case there is the possibility of recombination with their species. The viscosity of the solvent medium changes the initiator activity. The intensity of the lattice effect increases with increasing viscosity of the medium. Another factor affecting the initiator yield varies with the monomer type. In this study, the styrene polymerization was controlled in the presence of *g*-CTA. In calculating the theoretical molecular weights, the initiator efficiency was taken as $f = 0.5–0.6$, considering the steric hindrance of the graft macro xanthate agent. The molecular weights' evolution of all three graft copolymers was found to be in good agreement between gel permeation chromatography and calculated values. The GPC chromatogram shown in Fig. 2a, b for the PVA-g-PS graft copolymer exhibits a single-mode and narrow peak, indicating that no side reactions occur during syntheses.

Synthesis of macro-MADIX agents containing polyvinyl alcohol (PVA)-based benzoyl-derived xanthate group

The chemical structure of g-CTA1-3 was verified by FTIR, ^{1}H NMR and ^{13}C NMR. The FTIR spectra of MADIX

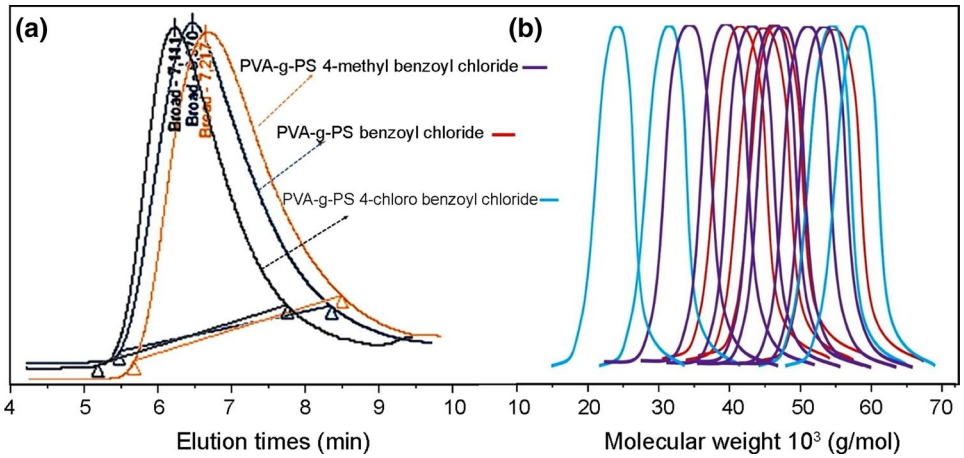


Fig. 2 **a** GPC traces of PVA-g-PS derivates, and **b** GPC traces of PVA-g-PS graft copolymer with molecular weight increase

agents as shown in Fig. S1, S2 and S3 are compared with the FTIR spectrum of the PVA-6000 in Fig. S4. The –OH groups of PVA-6000 at 3500–3200 cm^{-1} disappeared in the FTIR spectra of g-CTA1-3. FTIR spectroscopy of MADIX agents showed peaks of C = S groups at 1200–1010 cm^{-1}, and C = O groups indicated peaks at 1715–1675 cm^{-1}, $–CH_2$ protons at 1–2 ppm in the ^1H NMR spectra of *g*-CTA 1 in Fig. S5, protons bound to the benzene ring ($-CH_3$) at 2.5 ppm and -CH protons belonging to the aromatic structure were obtained in 7.5–8 ppm. Peaks of macro *g*-CTA in the ^{13}C NMR spectra of $–CH_2$ groups at 40 ppm, -OCH groups at 75 ppm, –CH groups on aromatic rings at 125–130 ppm, C = O groups at 135 ppm, C = S groups at 165–170 ppm can be seen in Figs. S6, S7 and S8.

The macro-g-CTA was acquired by the termination reaction of the PVA-xanthate salts obtained from the reaction of PVA with CS_2 and KOH by aromatic acyl chlorides. The xanthate salt and macro-g-CTA were precipitated in a 1:1 (v/v) mixture of diethyl ether and petroleum ether. The macro-g-CTA and the PVA were in the same mixture, and it was not possible to separate them by known techniques. The average molecular weight is given for the characterization of macromolecules. These are M_n by number and M_w by weight average molecular weights. If the values of M_n and M_w are close to each other, the chains length is equal.

The ln $[M]_o/[M]$ and PDI versus conversion (%) were plotted for all polymerization data. It has been observed that the molecular weight distribution of the polymers obtained by RAFT is quite narrow. The best-desired PDI value of the monodisperse distribution is considered to be 1.00 [36, 37]. Our obtained PDI values from MADIX polymerizations changed from 1.15 to 1.47. The controllability of the graft copolymerization was confirmed by the low PDI of the resulting copolymer.

Copolymerization of styrene with macro *g*-CTA 1

The polymerization conditions and results of the synthesized graft copolymer are given in Table 2, and the FTIR spectra for g-CTA 1 and PVA-g-PS are presented in Figs. S1 and S9, respectively. ^1H NMR is given in Fig. S5 for g-CTA 1 and in Fig. S10 for PVA-g-PS, and ^{13}C NMR is given in Fig. S6 for g-CTA 1. GPCs are monitored in Fig. S11 and DSC is shown in Fig. S12. PVA-g-PS characteristics show that the amount of polymer, molecular weight, and ln $[M]_o/[M]$ increases with conversion (%) (Fig. 3). PDI values changed between 1.31 and 1.45. According to Mn_{GPC} and Mn_{Theo} versus conversion (%) graph for PVA-g-PS, the monomer conversion increases linearly (Figs. 4 and 5). When PVA-6000 benzoyl chloride macro-MADIX agent is used for styrene polymerization, it is seen that the molecular weight control is good.

Table 2 PVA-g-PS characteristics obtained for graft copolymerization of styrene with macro-g-CTA 1 at 60 °C

Code	Time (h)	Yield (g)	Mn_{GPC} (g/mol)	Mn_{Theo} (g/mol)	ln $[M]_o/[M]$	$PDIM_W/M_n$	% Conversion
S-1	24	0.1352	39.594	41.582	0.1610	1.45	15
S-2	96	0.2433	40.744	44.528	0.3115	1.45	27
S-3	144	0.3466	43.303	46.657	0.4801	1.38	38
S-4	168	0.4704	44.283	49.746	0.7287	1.40	52
S-5	216	0.6147	51.842	54.160	1.1277	1.31	72

Temperature 60 °C, DMSO 1.5 mL, RAFT agent 0.01594 g, St 0.909 g, AIBN 0.02 g

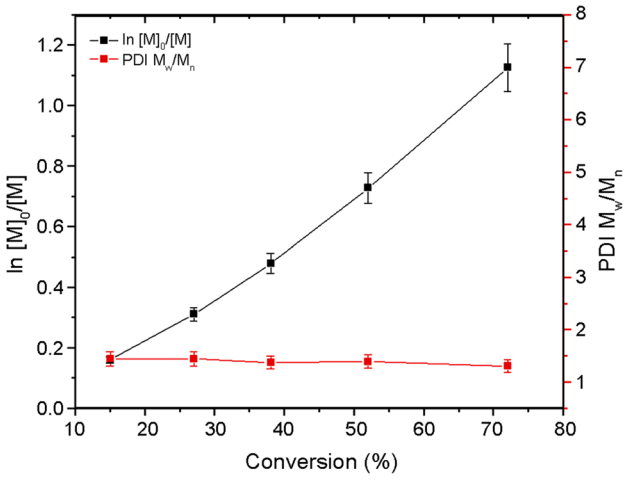


Fig. 3 In[M]$_o$/[M] and PDI values versus conversion (%) plots for styrene graft copolymerization macro g-CTA 1 agent at 60 °C

Reaction kinetics was observed as pseudo-first-order rate ($k_{app} = 5.1 \times 10^{-3}$ s^{-1}).

Copolymerization of styrene with PVA-6000 *p*-tolyl chloride macro-MADIX agent

The reaction conditions and results related to synthesis are given in Table 3. The FTIR spectra for g-CTA 1 and PVA-g-PS are presented in Figs. S2 and S13, respectively. The.^{1}H NMR spectra of g-CTA 1 and PVA-g-PS are shown in Figs. S14 and S15, respectively. The ^{13}C NMR spectrum in Fig. S7 belongs to g-CTA 1. The GPC and DSC results are given in Figs. S16 and S17, respectively. Molecular weight distribution, PDI and ln [M]$_o$/[M] increased with conversion (%) (Fig. 6). PDI values changed between 1.34 and 1.47.

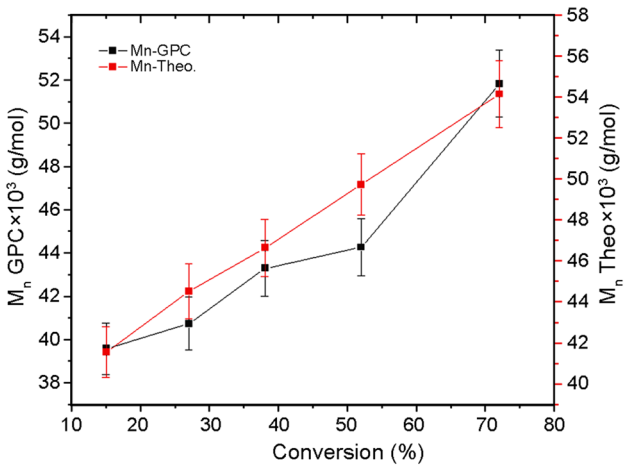


Fig. 4 Mn_{GPC} and Mn_{Theo} versus conversion (%) graph for styrene graft copolymerization with macro-g-CTA 1at 60 °C

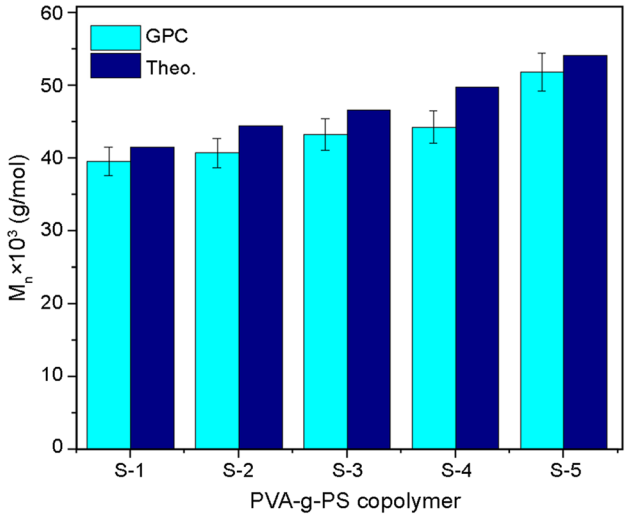


Fig. 5 Theoretical PVA-g-PS and GPC molecular weight comparison graph in presence of macro-g-CTA 1

The observed molecular weight (GPC) increase is compatible with the theoretically calculated values. According to Figs. 7 and 8, the monomer conversion increased linearly. The results confirmed that molecular weight control was provided well in styrene polymerization with PVA-6000 *p*-tolyl chloride macro-MADIX agent. Reaction kinetics was observed as pseudo-first-order rate ($k_{app} = 2.8 \times 10^{-2}$ s^{-1}).

Copolymerization of styrene with PVA-6000 4-chlorobenzoyl chloride macro-RAFT agent

The polymerization conditions and results related to the synthesis are given in Table 4. The FTIR spectra shown in Figs. S3 and S18 belong to g-CTA 1 and PVA-g-PS, respectively. The ^{1}H NMR spectra of g-CTA 1 and PVA-g-PS are shown in Figs. S19 and S20, respectively. The ^{13}C NMR spectrum in Fig. S8 belongs to g-CTA 1. The GPC and DSC results are given in Figs. S21 and S22, respectively. It is seen that the amount of ln [M]$_o$/[M] increased by the conversion (%), and the ratio of PDI decreased over conversion (%) (Fig. 9). PDI values changed between 1.23 and 1.40. The molecular weights increased linearly with monomer consumption according to the conversion (%) graphs shown in Figs. 10 and 11. It has been observed that the design of MADIX agent with the benzoyl chloride, *p*-tolyl chloride, and 4-chlorobenzoyl chloride selected as R group and the activation in the restart of the reaction were obtained successfully. Low PDI values were obtained by the reaction extension conversion (%) in molecular weight control of three MADIX agents. Reaction kinetics was observed as pseudo-first-order rate ($k_{app} = 1.7 \times 10^{-2}$ s^{-1}).

The aromatic ring groups of the -C = CH bond structure appeared at about 3067–2088 cm^{-1} on the FTIR

Table 3 PVA-g-PS characteristics obtained for graft copolymerization of styrene with macro-g-CTA 2 at 60 °C

Code	Time (h)	Yield (g)	M_{GPC} (g/mol)	M_{Theo} (g/mol)	ln $[M]_o/[M]$	$PDIM_W/M_n$	% Conversion
AS-1	10	0.0602	37.532	40.757	0.0685	1.47	7
AS-2	14	0.1986	42.337	44.094	0.2465	1.43	22
AS-3	20	0.2658	45.779	45.874	0.3458	1.38	30
AS-4	22	0.3010	48.482	46.542	0.4021	1.34	33
AS-5	26	0.3665	50.066	48.322	0.5161	1.33	41
AS-6	30	0.3788	52.674	49.767	0.5390	1.29	43
AS-7	32	0.4495	55.327	51.438	0.6822	1.27	50

Temperature 60 °C, DMSO 1.5 mL, RAFT agent 0.01594 g, St 0.909 g, AIBN 0.02 g

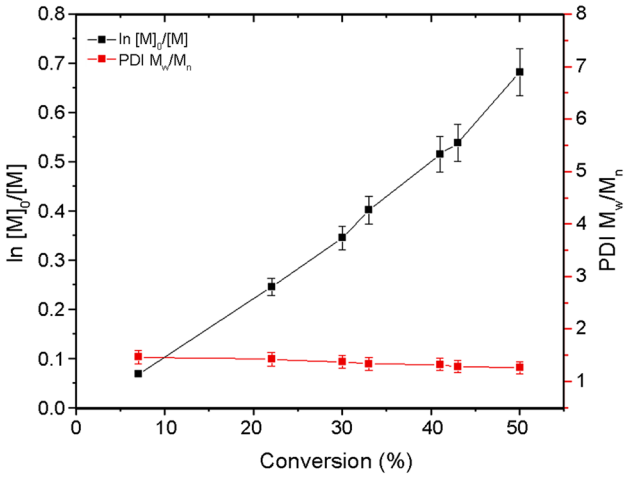


Fig. 6 Mn_{GPC}-PDI-conversion (%) graph for styrene MADIX polymerization with macro-g-CTA 2

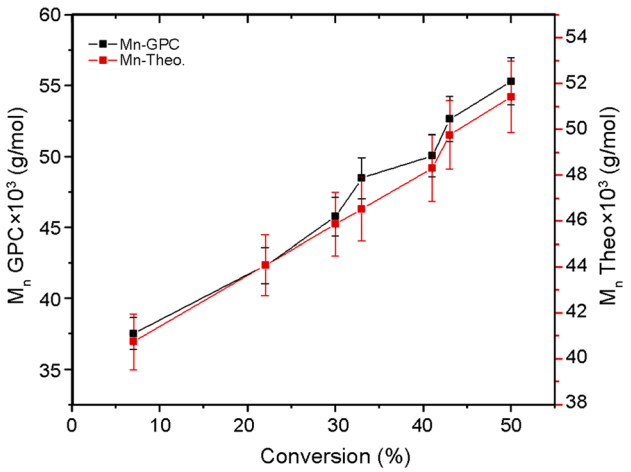


Fig. 7 Mn_{GPC} and Mn_{Theo} versus conversion (%) graph for RAFT polymerization of styrene with macro-g-CTA 2

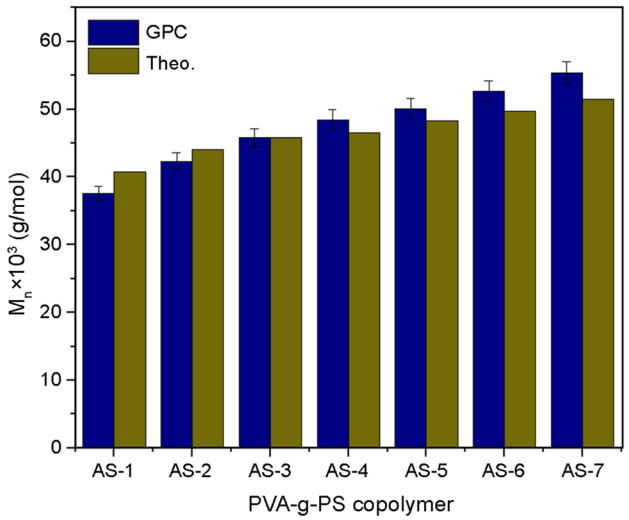


Fig. 8 Theoretical PVA-g-PS and GPC molecular weight comparison graph in presence of macro g-CTA 2

spectrum and the peaks at around 2000–1600 cm^{-1} and 1200–1010 cm^{-1} indicated the -C = S groups. The 1715–1675 cm^{-1} peaks represent the C = O group. In the ^1H NMR spectra of poly (PVA-*g*-St) graft copolymers, $-CH_2$ protons are observed at 1–1.5 ppm, –CH protons at 2.9 ppm and 6.2–7.3 ppm, the peaks of –CH protons in the aromatic ring of styrene structure at 7.4 ppm, and $–CH_3$ protons bound to the aromatic ring in the *p*-tolyl structure at 2.7 ppm.

The DSC results of the synthesized PVA-g-PS copolymers are presented in Figs. S12, S17 and S21. The glass transition temperature (T_g) of the PVA-6000 polymer is 85 °C. The addition of the styrene block of the PVA-g-PS graft copolymer increased the T_g value up to 100 °C. Melting temperature (T_m) is 131 °C for benzoyl chloride due to the increase in the amount of branching and molecular weight increase of the macromolecule. The values obtained are consistent with the other studies reported [1, 2, 8]. The glass transition temperature varies depending on the number of branches and graft length. Moreover, considering the

Table 4 PVA-g-PS characteristics obtained for graft copolymerization of styrene with macro-g-CTA 3 at 60 °C

Code	Time (h)	Yield (g)	M_{GPC} (g/mol)	M_{Theo} (g/mol)	ln $[M]_o/[M]$	$PDIM_W/M_n$	(%) Conversion
A-1	6	0.1720	39.742	46.173	0.2097	1.40	19
A-2	22	0.2916	46.404	49.071	0.3868	1.39	33
A-3	30	0.3469	58.628	50.313	0.4806	1.23	39
A-4	32	0.4322	59.695	52.383	0.6452	1.23	49

Temperature 60 °C, DMSO 1.5 mL, RAFT agent 0.01594 g, St 0.909 g, AIBN 0.02 g

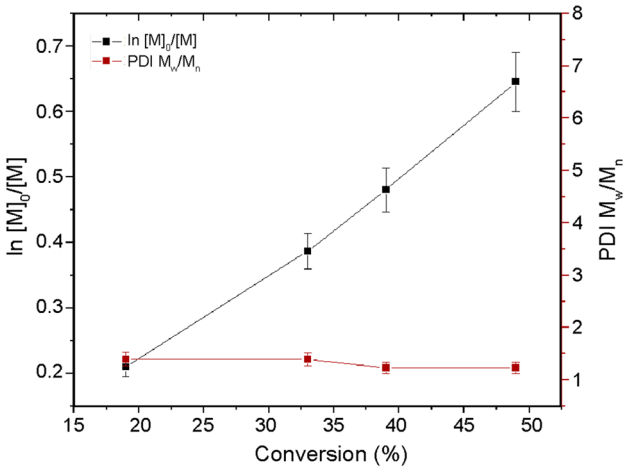


Fig. 9 $\ln[M]_o$ / [M] and PDI versus conversion (%) graph for styrene MADIX polymerization with macro g-CTA 3. [St]/[*g*-CTA3]/[AIBN] = 1000/9.7/1.6

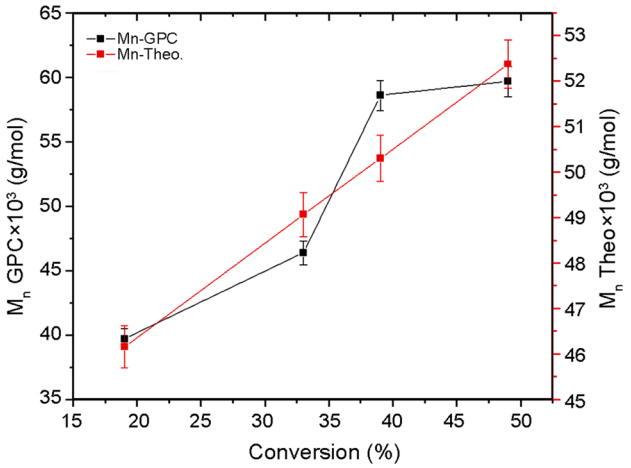


Fig. 10 Mn_{GPC} and $Mn_{Theo.}$ versus conversion (%) graph for styrene MADIX polymerization. [St]/[g-CTA3]/[AIBN] = 1000/9.7/1.6

hydrodynamic volume of the macromolecule, temperature differences occur between the glass transition temperature and the melting temperatures. It is seen that T_g 105 °C and

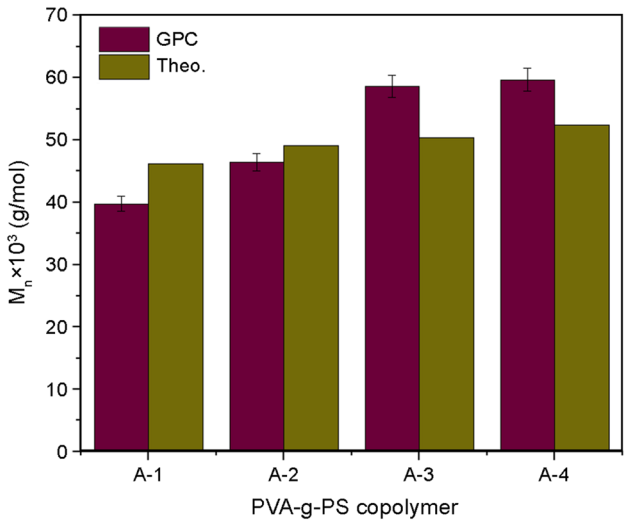


Fig. 11 Theoretical PVA-g-PS and GPC molecular weight comparison graph in presence of macro-g-CTA 3

T_m 154 °C for PVA-6000 benzoyl chloride, and T_g 110 °C and T_m 157 °C for PVA-6000 benzoyl chloride.

Conclusion

To summarize, macro-MADIX agents were synthesized over the polyvinyl alcohol chain through MADIX techniques. Well-defined PVA-g-PS graft copolymers were synthesized by controlled polymerization of xanthate MADIX chain transfer agent and styrene using AIBN initiators. It was concluded that benzoyl chloride derivatives were effectively reversibly separated and recombined. The graft copolymers showed narrow molecular weight distribution and PDI ratios between 1.2 and 1.4 obtained by GPC analysis. Macro-MADIX agent was used in different conditions (such as initiator, amount of monomer, and reaction time), and novel PVA-g-PS graft copolymers were synthesized. The molecular weight distribution of the graft copolymers increased over conversion (%) in a controlled manner, and low PDI values were determined. Furthermore, it was observed that the design of MADIX agent with the benzoyl chloride,

p-tolyl chloride and 4-chloro benzoyl chloride was selected as R group, and the activation in the restart of the reaction was found to be effective. Low PDI values were obtained by the reaction extension conversion (%) in molecular weight control of three MADIX agents. The polymerization was carried out by the MADIX agent, which was synthesized by benefiting from the branching feature of polyvinyl alcohol, which also provided an easy and fast synthesis of block copolymers.

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