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Synthesis of PMMA-b-PEG-b- PMMA by controlled Polymerization Using Macro-RAFT Agents

Mehmet BAĞLAN[1], Ümit YILDIKO[2], İsmail ÇAKMAK[1], Ahmet Turan TEKEŞ[1]

ABSTRACT: In this work controlled radical polymerization (CRP) of methyl methacrylate was carried out in the presence of the Poly(ethylene glycol)(PEG) xanthate reversible addition fragmentation (RAFT) chain transfer agent designated as (CTA_1) and (CTA_2). Firstly, PEGs having different molecular weights (400 and 600 g/mol) were reacted KOH and CS_2 and the terminated 4-chloro benzoyl chloride to obtain PEG-xathates. RAFT agent possessing PEG chain was used in the RAFT polymerization of MMA to yield PMMA-b-PEG-b-PMMA tri-block copolymers which can be used in various potential applications. With the gravimetric follow of the reaction, the control mechanism works well and the molecular weight has grown linearly. The structures of the synthesized macro RAFT agents and polymers were characterized by ^{1}H-NMR, ^{13}C-NMR and FT-IR spectroscopic methods.

Key words: Block Copolymer, Controlled Radical Polymerization, Polyethylene Glycol, RAFT

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[1] Mehmet BAĞLAN (0000-0002-7089-7111), İsmail ÇAKMAK (0000-0002-3191-7570), Ahmet Turan TEKEŞ (0000-0002-9942-7367) Kafkas University, Department of Chemistry, Kars, Turkey

[2] Ümit YILDIKO (0000-0001-8627-9038), Iğdir University, Tuzluca Vocational High School, Iğdir, Turkey
Sorumlu yazar/Corresponding Author: Ümit YILDIKO, yildiko1@gmail.com

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INTRODUCTION

The properties of the polymers can be changed with the aid of functional groups at the ends of the polymerization (Gu, Xu et al., 2014). This change is usually achieved either by the use of the functional group in initiating the other polymerization or by reaction with polymers having another compatible function (Barsbay and Güven 2018). Because of this reason, intensive studies have been carried out in recent years by means of polymerization methods which have well defined, and some *narrow* molecular weight and allow the desired functional groups have been added to the structure because of controlled polymerization of polymers. (Hemp, Smith et al., 2014, Ma'Radzi, Sugihara et al., 2014, Li, Ding et al., 2017).

Independed radical polymerization; is a polymerization carried out on easy experimental conditions, in which most of the vinyl monomers can be polymerized with the most industrial applications(Yan, Lin et al., 2017, Liu and Hobbs 2018). Despite all the advantages described above, it is not possible to control the molecular weight, the molecular weight distribution and to obtain polymers prepared at the desired molecular weight in the chain architecture(Beija, Marty et al., 2011). However, by using the case of the living polymerization process it is possible to control and obtain various block copolymers having narrow polydispersity and different chain structure (Foster, Radzinski et al., 2015, Sütekin and Güven 2018).

Among the controlled / living radical polymerization techniques discovered in the last twenty years, nitroxide-mediated polymerization ATRP(Neugebauer 2015, Chmielarz 2016, Liu and Hobbs 2018), nitroxide-mediated polymerization, NMP (Nicolas, Guillaneuf et al., 2013, Kermagoret and Gigmes 2016, Ballard, Aguirre et al., 2017)and reversible addition-removal chain transfer (RAFT) (West, Barner-Kowollik et al., 2010, Yeole and Hundiwale 2011, Ma'Radzi, Sugihara et al., 2014, Sütekin and Güven 2018)polymerization techniques have been used extensively in molecular architecture design. Sensitive polymer very well-defined displaying Molecular weight distributions, high end group suitability and various complex architectures are unique for the synthesis of materials. Unlike ATRP or NMP, the RAFT technique does not progress with a reversible termination reaction but is based on a degenerative chain transfer process to provide control. RAFT is defined as one of the most versatile CRP processes because of the availability of virtually all vinyl monomer types, tolerance to various solubilizers and initiators, and (mini-) heterogeneous media such as emulsion or suspension(Yang, Luo et al., 2009, Gu, Xu et al., 2014). RAFT agent modification can be used to synthesize branched polymers, multi-block, graft, comb or star block copolymers with unique physical properties through chain extension reactions on polymer blocks(Hemp, Smith et al., 2014, Fu, Lei et al., 2017).

In our study, two advantages are offered in terms of synthesis chemistry. The first is the synthesis of RAFT agent containing diblock difunctional polyethylene glycol (PEG), the second is the tri-block copolymer synthesis in which the molecular weight distribution is homogeneous with controlled chain extension. There is little research in the literature with RAFT polymerization for block copolymers using PEG Macro RAFT agents. We anticipate that novel studies will contribute to create infrastructure for creating infrastructure for the preparation of block copolymers with high economic efficiency, preparation of new health, cosmetics and nano technological materials (West, Barner-Kowollik et al., 2010, Fu, Lei et al., 2017).

MATERIALS AND METHODS

Synthesis of Difunctional Macro Xanthate RAFT Agents: RAFT agents are obtained result of terminating the PEG with aromatic acyl chlorides from the PEG-xanthate salts obtained in the reaction with CS_2 and KOH. A series of difunctional xanthate Macro RAFT agents using PEG-400, PEG-600 were prepared as described by Kartal et al., then synthesized according to the reaction given in Fig.1. The overall reaction of the synthesized xanthate Macro RAFT agents is shown in Fig 1.(Kartal et al., 2014)

PEG-400 4-chlorobenzoyl Chloride Macro Xanthate RAFT Agent : ^{1}H-NMR (CDCl3, δ, ppm): 8.0–7.6 (4H, ArH), 4.4 (2H, -OCH2), 3.7–3.4 (4H, –CH2CH2–), ^{13}C-NMR (CDCl3, δ, ppm): 168 (1C, –C=S), 164 (1C, C=O), 143 (1C, C- CH3,), 133-127 (6C, Ar), 72 (2C, O– CH2), 60 (2C, –CH2CH2–). FT-IR (n, cm-1): 3069 (–C–H, Ar), 1674 (CHO) 1086 (– C=S).

PEG-600 4-Chlorobenzoyl Chloride Macro Xanthate RAFT Agent: ^{1}H-NMR (CDCl3, δ,ppm): 8.0–7.6 (4H, ArH), 4.4 (2H, OCH2), 3.7–3.4 (4H,CH2CH2–), ^{13}C-NMR (CDCl3, δ,ppm): 168 (1C, –C=S), 164 (1C, C=O), 143 (1C, C–CH3,), 133–127 (6C,Ar), 72 (2C, O–CH2), 60 (2C, –CH2CH2–). FT-IR(n, cm-1): 3069 (–C–H, Ar), 1674 (–C=O) 1086(–C=S).

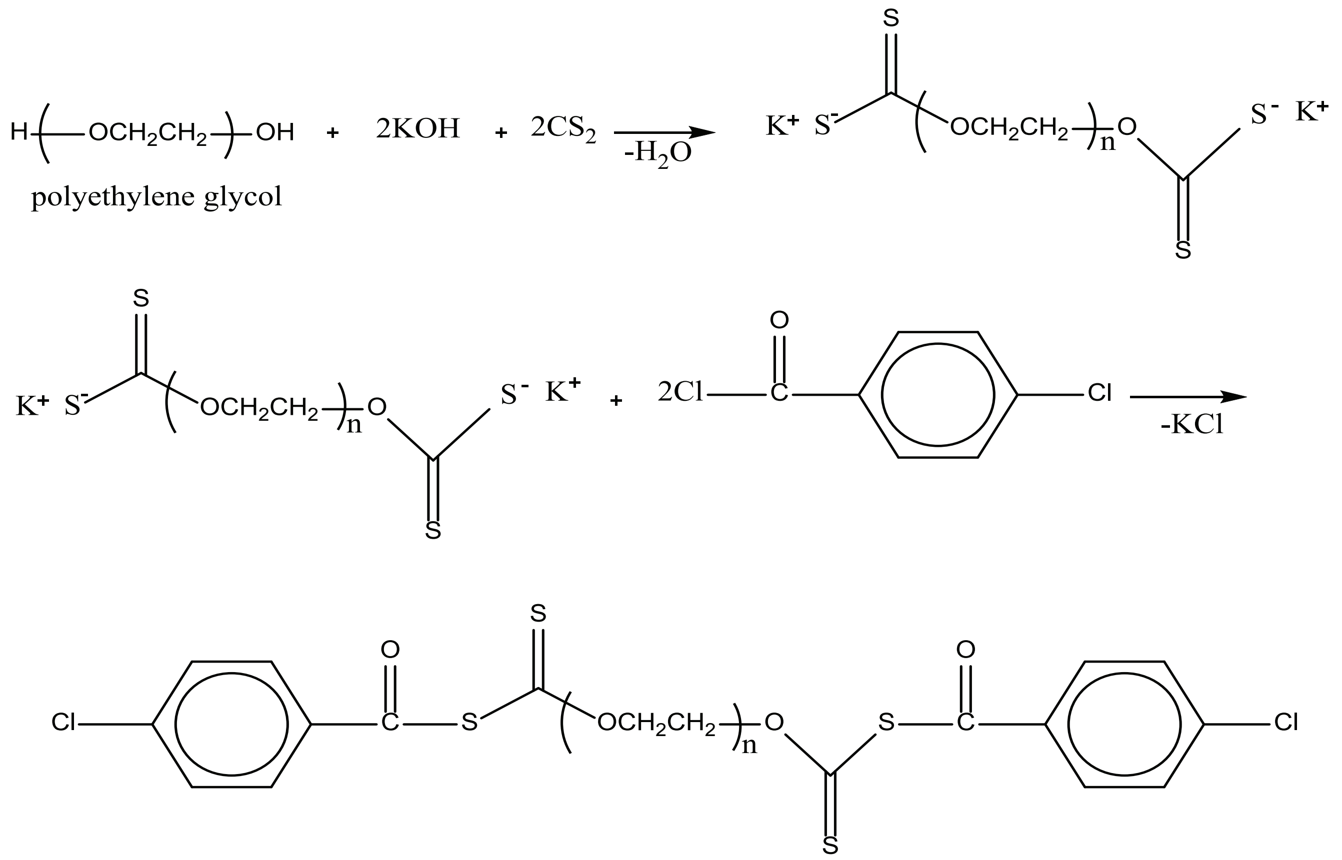

Figure 1. General Synthesis Reaction of Xanthate Macro RAFT Agents

Polymerization of Difunctional Macro Xanthate RAFT Agents with Methyl Methacrylate: The methyl methacrylate polymerization results of the synthesized macro xanthate RAFT agents resulted in block copolymers of PMMA-b-PEG-b-PMMA in different molecular weights. For general polymerizations, [Monomer] was taken as [RAFT agent]: [AIBN] 1000: 8: 1.6. The general polymerization reaction is shown in Figure 2.

Polymerization of PEG-400 4-Chlorobenzoyl Chloride Macro Xanthate RAFT Agent with Methyl Methacrylate: 0.02637 g ($1.606 x 10^{-4}$ mol) of AIBN was taken in a beaker and dissolved in 9 mL of benzene. 9 mL of distilled methyl methacrylate was stirred over a brief period. This solution was passed through an argon gas to prepare an inert condition. 0.477 g ($6,3002 x 10^{-4}$ mol) of PEG-400 4-chlorobenzoyl chloride Macro RAFT agent was added and mixed well to prepare the stock solution. The remaining 18 mL of solution was taken up with 2 mL of each tube and the solutions were again purged with Ar gas and the tubes were capped and sealed thoroughly with paraffin before being allowed to polymerize in a beaker with silicone oil inside at 75°C.Each tube was taken for 2 hours and precipitated in a beaker containing methanol. Methanol was completely pulled up for the air and allowed to stand in the oven, and the resulting sample was dried in a vacuum oven, and at the end it was transferred into a desiccator until reaching a constant weighing. The experiment reaction is shown in Figure 2. FT-IR(n, cm-1): 3069 (–C–H, Ar), 1674 (–C=O) 1086(–C=S).

PEG-600 4-Chlorobenzoyl Chloride Polymerization of Macro Xanthate RAFT Agent with Methyl Methacrylate: 0.0262 g ($1.596 x 10^{-4}$ mol) of AIBN was taken in a beaker and dissolved in 9 mL of benzene. 9 mL of distilled methyl methacrylate was stirred over a brief period. This solution was passed through an argon gas to make the medium inert.0.598 g ($6.3002 x 10^{-4}$ mol) of PEG-600 4-chloro benzoyl chloride Macro RAFT Agent was added to the solution and mixed well.

The remaining 18 mL of solution was taken up with 2 mL of each tube and the solutions were again purged with Ar gas and the tubes were capped and sealed thoroughly with paraffin before being allowed to polymerize in a beaker with silicone oil inside at 75 °C. Each tube was taken for 2 hours each and precipitated in a beaker containing methanol. Methanol was completely pulled up to the air and allowed to stand in the oven, and the vacuum was dried in a desiccator until reaching a constant weighing (Figure 2). FT-IR (n, cm-1): 3069 (–C–H, Ar), 1674 (CHO) 1086 (– C=S).

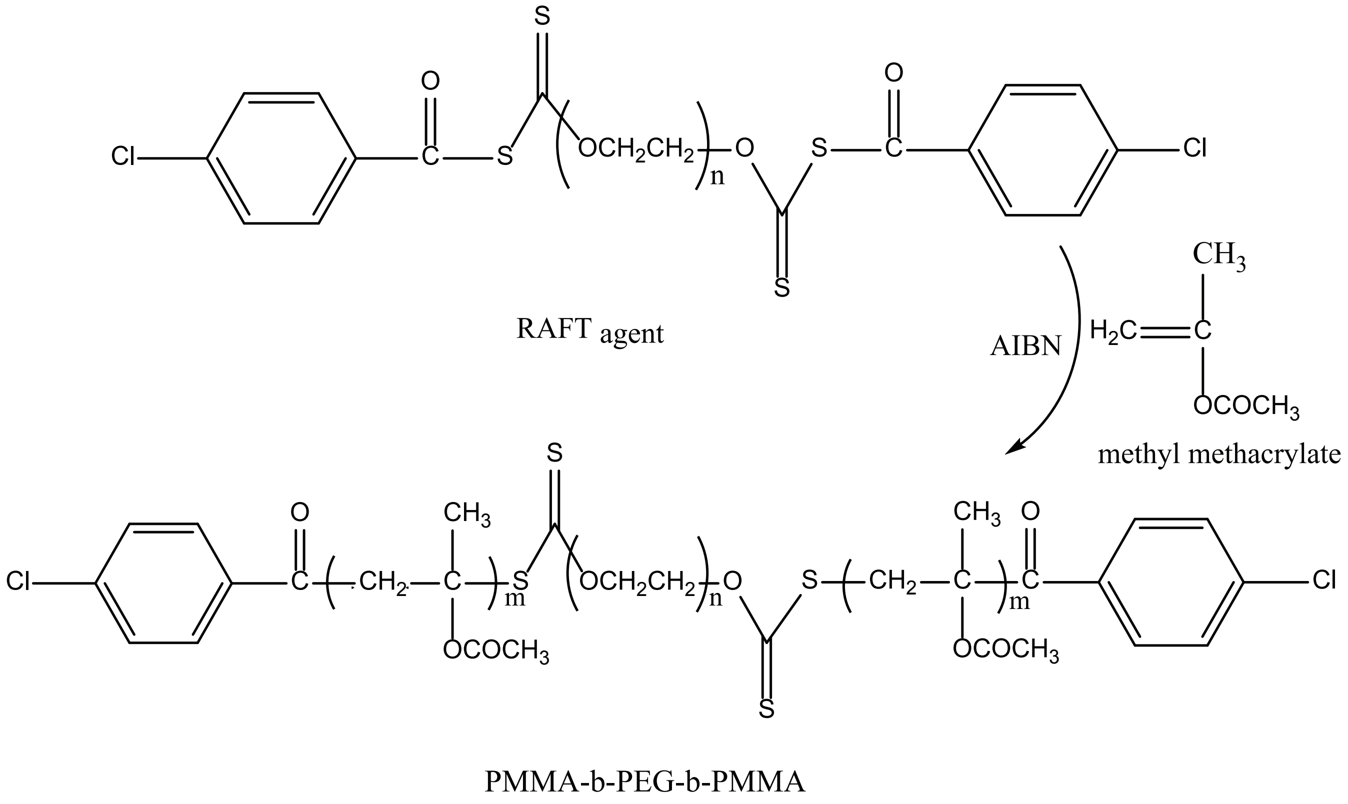

Figure 2. General Formation Reaction of PMMA-b-PEG-b-PMMA Block Copolymers

RESULTS AND DISCUSSION

Polymerization of Macro RAFT Agents Containing Polyethylene Glycol (PEG) Based Benzoyl Derivative Xanthate Group with Methylmethacrylate: The experiment results showed that the molecular weight distribution of the polymers obtained by RAFT polymerization is very narrow.

The ln [M]o / [M] -Remaining Graph drawn for all polymerisation data, Mn Theoretical -% Monomer Transformation, Mn Theoretical-Time Graph, Monomer Transformation-Time Graphs were drawn using OriginPro 8 program.

Polymerization of PEG-400 4-Chlorobenzoyl Chloride Macro RAFT Agent with Methylmethacrylate: The reaction conditions and results for the synthesis of the polymerization of PEG-400 4-chlorobenzoyl Chloride Macro RAFT agent (CTA_1) with methyl methacrylate are given in table 1.

When we observe Table 1, we can clearly see that the weight of polymer was increased over time (Figure 3).

We saw that there is a linear increase by taking Mn theoretical-time values (Figure 4). We observed that monomer conversion increased linearly with Monomer Transformation-Time graph (Figure 5).

As a result, it is seen that molecular weight control is provided when the tables and graphs of PMMA-b-PEG-b-PMMA block copolymer obtained are examined.

Table 1. Polymerization Data of PEG-400 4-chlorobenzoyl chloride Macro RAFT Agent with Methylmethacrylate

Experiment N.	Experiment code	Experiment Time (h)	Polymer (g)	ln $[M]_o/[M]$	M_n Theoric (g/mol)	Yield %
1	MM-1	2	0.5165	0.51	10923	39.73
2	MM-2	4	0.6889	0.76	14290	52.99
3	MM-3	6	0.7293	0.82	15080	56.10
4	MM-4	8	0.9480	1.31	19352	72.92
5	MM-5	10	1.2456	3.07	25165	95.81
6	MM-6	12	1.2518	3.25	25287	96.29
7	MM-7	14	1.2867	4.87	25968	98.97

Table 1 gives the results of the experiment conducted about CTA_1. As seen in Table1 the RAFT agent was introduced into the polymerization from the initial stage of polymerization and oligomers were formed by adding monomer at both ends in the macro xanthate RAFT agent structure and the polymeric structure size increased linearly after 30 min - 60 min. This situation is confirmed by Figure3 and Figure4.In the later stages of the polymerization, the macro-RAFT agent appears to be sensitive and thus appears to result in a good control over the reaction. Since a portion of CTA_1 (chain transfer agent) is consumed prior to the start of RAFT polymerization, the ratio of effective monomer to RAFT agent ratio is increased and, as a result, the final polymer distribution will shift towards higher molar masses.

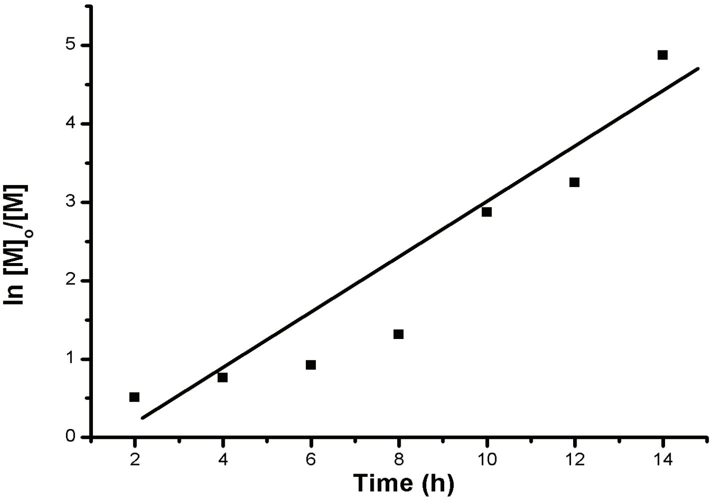

Figure3. Polymerization of PEG-400 4-Chlorobenzoyl Chloride Macro RAFT Agent with Methylmethacrylate ln [M] o / [M] -Time Graph

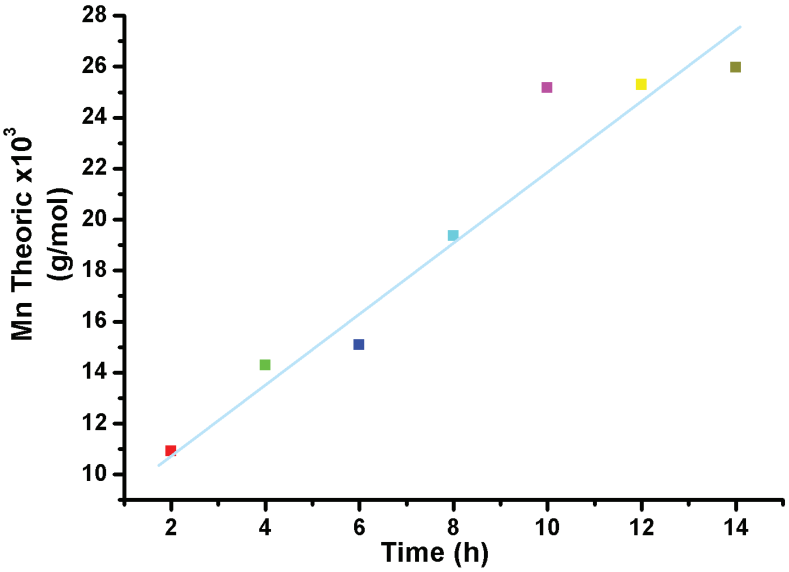

Figure 4. M_n Theoretical-Time Graph of Polymerization of PEG-400 4-Chlorobenzoyl Chloride Macro RAFT Agent with Methylmethacrylate

When experimental molecular weight (Mn theoretical) is plotted against monomer conversion, linear correlations have been observed indicating satisfactory controlled polymerization behavior. However, the linearity implies the value of incorporating the monomer into the polymer structure over time. (Figure 4). When the graph is examined, the conversion rate of the monomer consumed between 40% and 95% is stable while the addition of monomer after 95% is decreased.

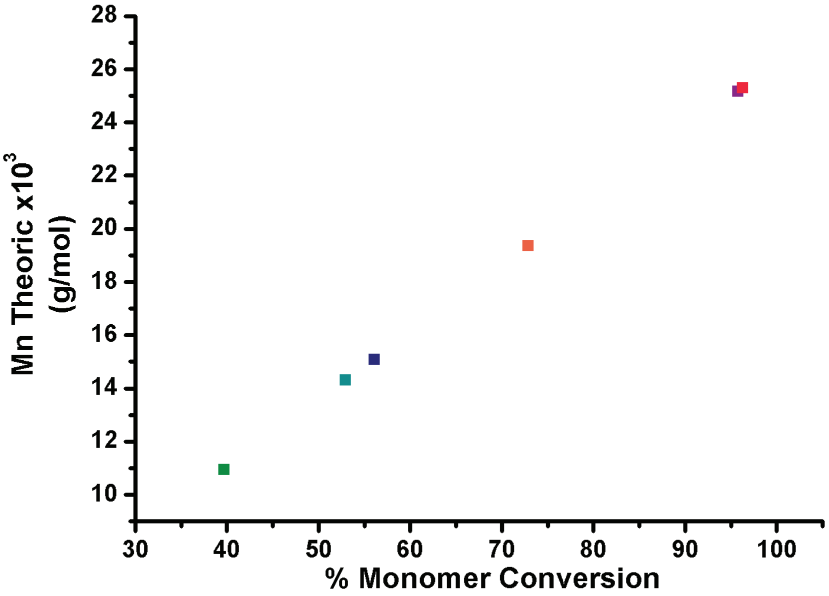

Figure 5. Mn Polymerization of PEG-400 4-Chlorobenzoyl Chloride Macro RAFT Agent with Methylmethacrylate-% Monomer Conversion

Nevertheless, according to a closer examination of Table 1, in all cases low distributions have been obtained, in other words, the deviation from linearity is small. Over time the increase in monomer conversion showed that the control in the molecular architecture is good. This situation is shown in Figure 6.

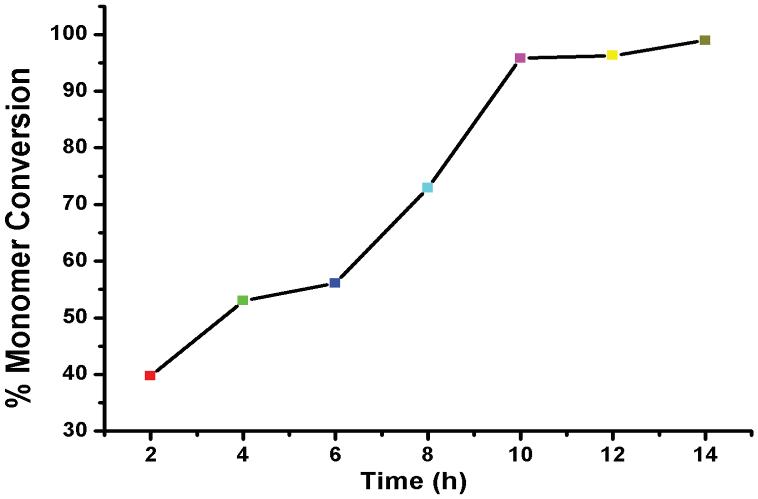

Figure 6. % Monomer Transformation-Time Graph of Polymerization of PEG-400 4-Chlorobenzoyl Chloride Macro RAFT Agent with Methylmethacrylate

Polymerization of PEG-600 4-Chlorobenzoyl Chloride Macro RAFT Agent with Methylmethacrylate: The reaction conditions and results for the synthesis of the polymerization of PEG-600 4-chlorobenzoyl Chloride Macro RAFT agent (CTA_2) with methyl methacrylate are given in Table 2. When we observe Table 2, we can see that the weight of polymer is increased over time (Figure 7). We can see that there is a linear increase by taking Mn theoretical-time values (Figure 8).

We observed that monomer conversion increased linearly with Monomer Transformation-Time graph (Figure 9). As a result, we can see that molecular weight control is provided when the tables and graphs of PMMA-b-PEG-b-PMMA block copolymer obtained are examined.

Table 2. Polymerization Data of PEG-600 4-chloro benzoyl chloride Macro RAFT Agent with Methylmethacrylate

Experiment N.	Experiment code	Experiment Time (h)	Polymer (g)	ln $[M]_0/[M]$	M_n Theoric (g/mol)	Yield %
1	MB-1	2	0.1825	0.20	5246	16.59
2	MB-2	4	0.2438	0.26	6660	22.16
3	MB-3	6	0.4450	0.60	11306	40.45
4	MB-4	8	0.6402	1.02	15814	58.20
5	MB-5	10	0.8150	1.71	19849	74.09
6	MB-6	12	0.9120	2.43	22086	82.90
7	MB-7	14	0.9215	2.51	22307	83.77
8	MB-8	16	0.9303	2.77	22511	84.57

When the values of Table 2 are examined (CTA_2), it is observed that the polymerization has been initiated from the initial stage and oligomer is formed by adding methylmethacrylate at both ends in macroxanthate RAFT agent structure and the polymeric structure dimension linearly increases after 1 - 3 hours. However, in the oligomer phase, which is more effective than the (CTA_2) agent (CTA_1) agent, it also provides control linearity. This situation is confirmed by Figure7 and Figure8.In the later stages of the polymerization, the macro-RAFT agent appears to be sensitive and thus results in good control of the reaction.

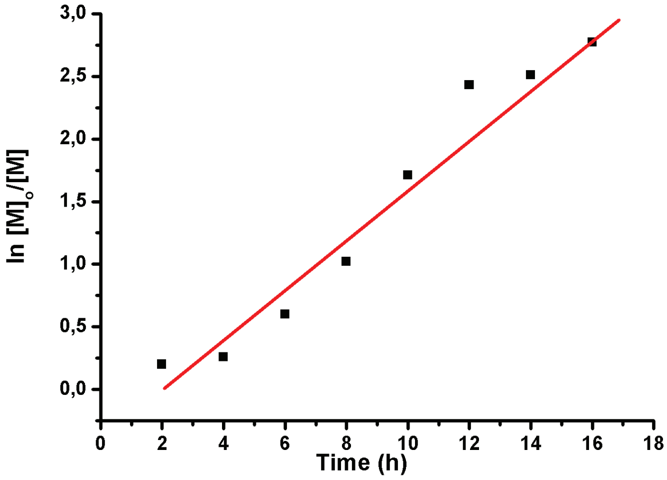

Figure 7. ln $[M]_0/[M]$ -time Graph of Polymerization of PEG-600 4-Chlorobenzoyl Chloride Macro RAFT Agent with Methylmethacrylate

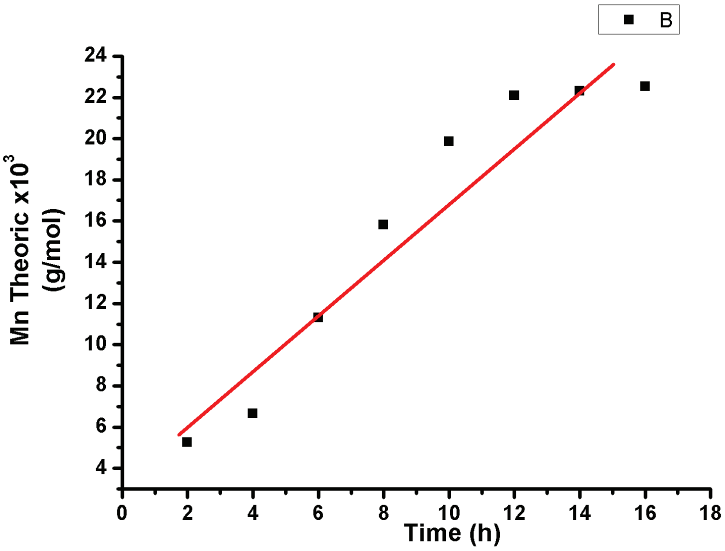

Figure 8. M_n Theoretical-time Graph of Polymerization of PEG-600 4-Chlorobenzoyl Chloride Macro RAFT Agent with Methylmethacrylate

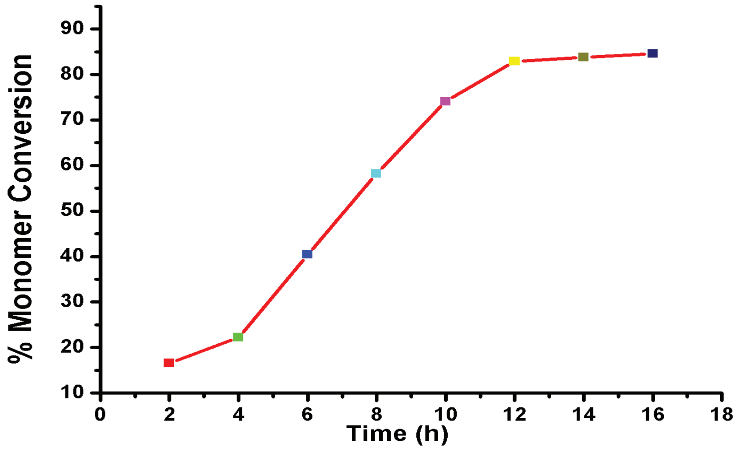

Figure 9. Monomer Transformation-time Graph of Polymerization of PEG-600 4-Chlorobenzoyl Chloride Macro RAFT Agent with Methylmethacrylate

When experimental molecular weight (Mn theoretical) is plotted against monomer conversion, a linear correlation has been observed indicating satisfactory and controlled polymerization behavior. Nevertheless, the linearity refers to the value of incorporating the monomer into the polymer structure over time. When Figures 9 and 10 are examined, the conversion rate of the monomer consumed between 20-90% is stable, whereas the addition of monomer after 90% is decreased.

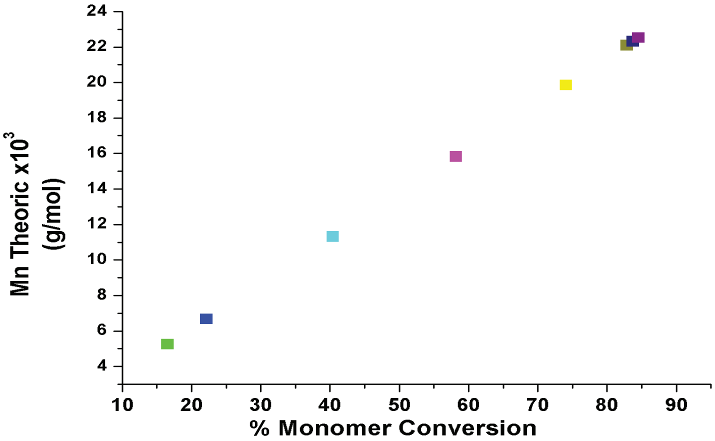

Figure 10. PEG-600 4-Chlorobenzoyl Chloride Macro RAFT Agent Polymerization with Methylmethacrylate Mn Theoretical-% Monomer Conversion

Synthesis of Macro RAFT Agents Containing Polyethylene Glycol (PEG) Based Benzoyl Derivative Xanthate Group: RAFT agents were formed by aromatic acyl chlorides of PEG-xanthate salts obtained from the reaction of PEG (400-600 g / mol) with CS_2 and KOH. Macro-RAFT agents were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The OH groups of PEG at 3500-3200 cm^{-1} when RAFT agents were compared with the PEG FT-IR spectra of the FT-IR spectra showed that the RAFT agents did not completely disappear in the FT-IR spectra and that the PEG did not react during the precipitation of the RAFT agent, it would have been impossible for us to distinguish between the known methods. FT-IR spectroscopy of RAFT agents showed C = S groups at 1200-1000 cm^{-1}, and C = O groups at 1720-1730 cm^{-1}

The protons of $-CH_2$ in 1-2 ppm in the ^{1}H-NMR spectra shown in figure11 and 12 of the RAFT agents, the protons of CH_3 in the benzene ring at 2.5 ppm, the -CH protons in the 4,5-5 ppm, -CH protons of the aromatic structure seen at 7-8 ppm are observed. The peaks at 13 ppm belong to PEG which co-precipitated with RAFT agent during precipitation. The structures of the peaksin Figure 11. confirm that situation explained above.

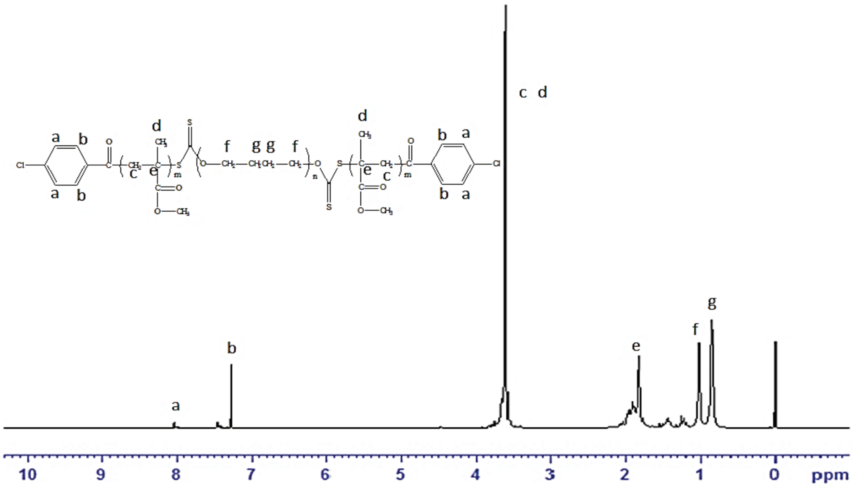

Figure 11.^{1}H-NMR Spectrum of Polymerization of PEG-400 4-chlorobenzoyl chloride Macro RAFT Agent with Methyl Methacrylate

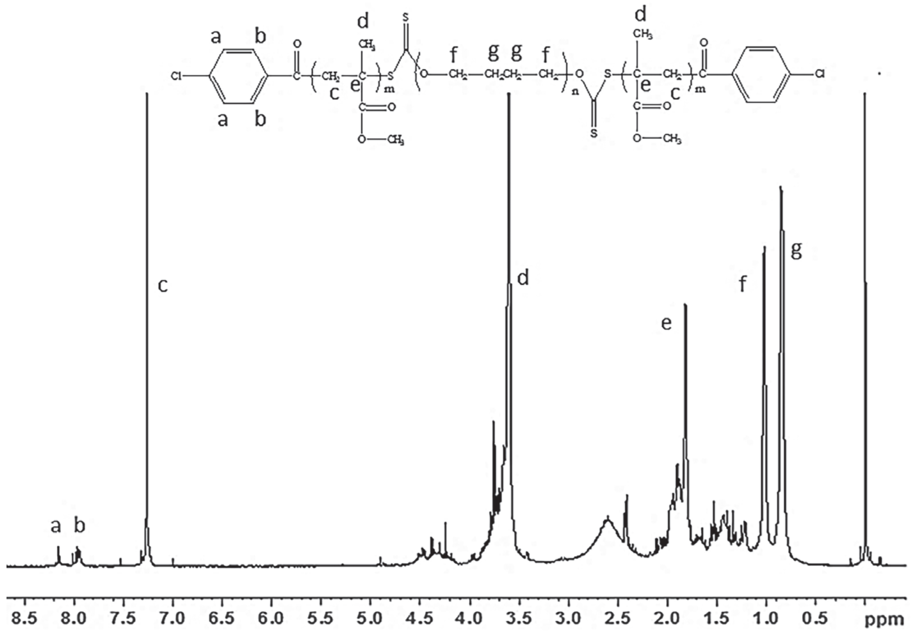

Figure 12.^{1}H-NMR Spectrum of Polymerization of PEG-600 4-chloro benzoyl chloride Macro RAFT Agent with Methyl Methacrylate

RAFT agents can be attached to -CH$_3$ groups attached to benzoyl chloride groups at 20 ppm, -CH$_2$ groups at 45 ppm, -CHO groups at the 80 ppm -OCH groups in the aromatic ring at -30 ppm, -CH groups in the aromatic ring at 80 ppm in the ^{13}C-NMR spectra shown in Figure 13. and 14. C = O groups at 135 ppm and C = S groups at 180 ppm are visible. The structures of the peaks that were seen were seen to confirm.

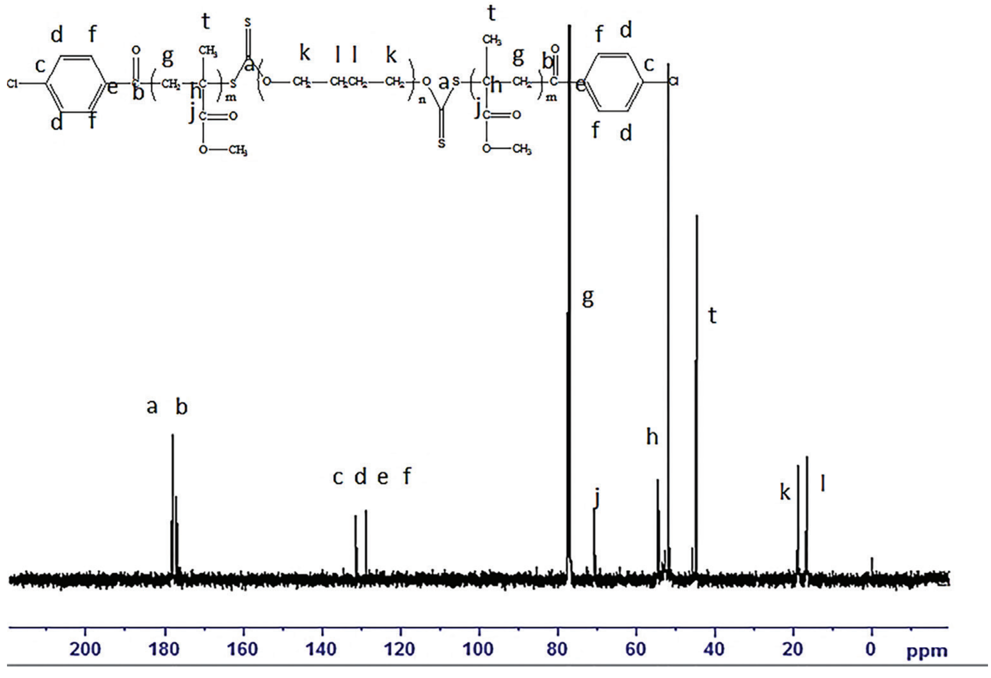

Figure 13. ^{13}C-NMR Spectrum of Polymerization of PEG-400 4-chlorobenzoyl chloride Macro RAFT Agent with Methyl Methacrylate

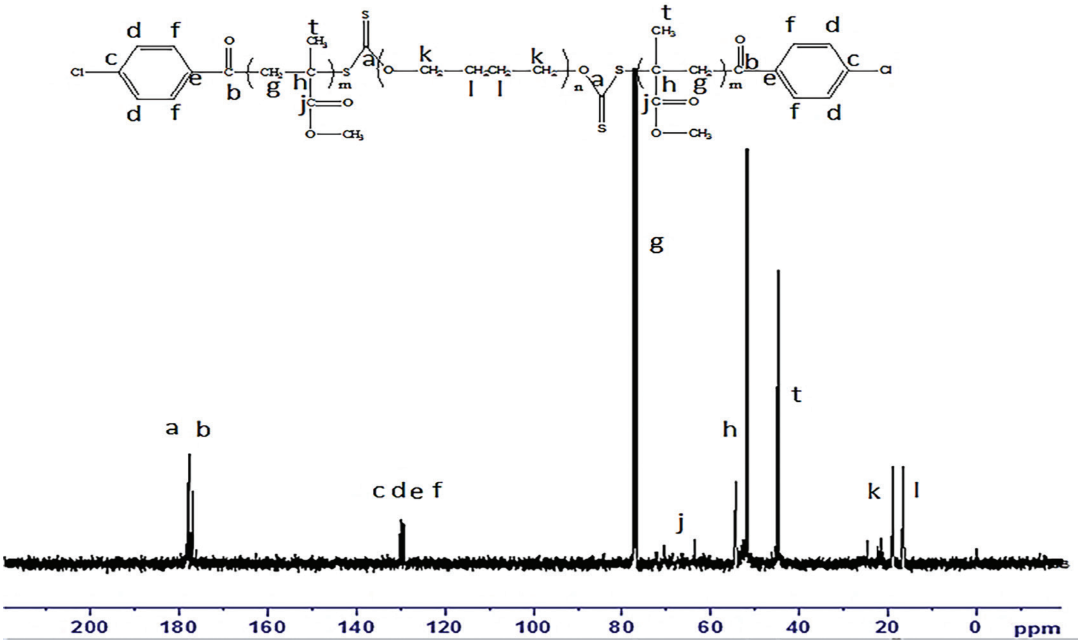

Figure 14. ^{13}C-NMR Spectrum of Polymerization of PEG-600 4-Chlorobenzoyl chloride Macro RAFT Agent with Methyl Methacrylate

RAFT agents; The end result of the PEG-xanthate salts obtained by reaction of PEG with CS_2 and KOH is terminated with aromatic acyl chlorides. The xanthate salt and RAFT agent were precipitated in a 1: 1 (v / v) mixture of diethyl ether and petroleum ether.

RESULTS

In this study, controlled block copolymers of PMMA-b-PEG-b-PMMA with narrow molecular weight distribution were synthesized using Macro xanthate RAFT agents synthesized. 4-Chlorobenzoyl chloride is attached in terms of chain end functionality. The success of RAFT polymerization depends on the activity of the synthesized RAFT agent. The activity of the R group was best provided by benzoyl chloride when compared to the 4-chloro benzoyl chloride derivatives. In general, the polymerization of macro-RAFT agents (CTA_1) and (CTA_2) methyl methacrylate with different molecular weights gives a good control of the RAFT agents in the polymerization in which the reaction time is generally short, and similarly long-term polymerizations make it more difficult to control. The resulting polymeric material is important in terms of industry and the use of many fields and the wealth of the literature.

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