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ORIGINAL PAPER

Synthesis and characterization of poly(ε-caprolactone-b-acryloyl chloride-g-vinyl chloride) ladder-type copolymer by "click" chemistry

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Abstract

The synthesis of poly(ε-caprolactone-b-acryloyl chloride-g-vinyl chloride) [poly(CL-b-AC-g-VC)] ladder-type copolymer was carried out by "click" chemistry of terminally azido poly(ε-caprolactone-b-acryloyl chloride) block copolymer (PCL-b-PAC-N_3) and terminally propargyl poly(vinylchloride) (PVC-propargyl). For this purpose, chain transfer agent (RAFT-ROP agent) was acquired by reaction of potassium salt of ethyl xanthogenate and the 5-bromo-2-hydroxybenzaldehyde. Poly(ε-caprolactone-b-acryloyl chloride) block copolymers was synthesized by a combination of reversible addition-fragmentation chain transfer polymerization (RAFT) of acryloyl chloride (AC) and ring-opening polymerization of ε-caprolactone (ε-CL) methods using chain transfer agent (RAFT-ROP agent) in one-step. Terminally azido poly(ε-caprolactone-b-acryloyl chloride) block copolymer (PCL-b-PAC-N_3) was synthesized by using poly(ε-caprolactone-b-acryloyl chloride) block copolymer and sodium azide. PVC-propargyl was obtained by the reaction of propargyl alcohol with polyvinyl chloride. By using PCL-b-PAC-N_3 and PVC-propargyl, ladder-type copolymer were also synthesized via "click" chemistry. The products were characterized comprehensively by ^{1}H-NMR, GPC, FT-IR and SEM. Thermal properties of the ladder-type copolymer were monitored by TGA and DSC methods. Spectroscopic and thermal analyses revealed that the reactions were successfully carried out.

Keywords "Click" chemistry · Ladder-type copolymer · Chain transfer agent · Reversible addition-fragmentation chain transfer polymerization · Ring-opening polymerization

Introduction

Modification of the polymers obtained after a successful polymerization process is an important task of macromolecular science. Today, it is particularly important not only to synthesize new types of plastic materials, but also to replace existing polymers to meet the requirements of new applications [1]. Copolymerization is one of the methods to improve polymer properties. The mix of two unique monomers, which has got different physical properties as well as chemical ones, leads to the formation of new materials in varying rates which is important both scientifically and commercially in the same polymer molecule [2–10]. Ladder polymers have made a rapid progress in the synthesis of organic optoelectronic materials thanks to their excellent properties without dissolution tendencies, high mechanical strength, good thermal stability and their unique fused structure [11–13]. Lately, the utilization of controlled / living radical polymerization techniques in the synthesis of complex macromolecules has immediately become widespread thanks to various monomers suitable for the technique and greater tolerance in experimental conditions in comparison with living ionic polymerization [14]. Reversible addition-fragmentation chain transfer polymerization technique (RAFT) is among the most extensively utilized techniques for controlled/living radical-polymerization (C/LRP) method and is an effective technique used for the macromolecular synthesis of a vast majority of well-identified polmers. The method is characterized as versatile thanks to its compatibility with a broad range of monomers and reaction conditions [15–29]. Moreover, Controlled ring-opening polymerization (ROP) is a widely used method for the polymerization of lactides and lactones. ROP is a unique polymerization process to produce a linear polymer by opening the cyclic monomer. Lactones have got such exclusive properties as biocompatibility, good mechanical properties, biodegradability, and notoxicity [30–36]. Thesedays, coppercatalyzed azide-alkynic cycloactivity (CuAAC) reaction, which is the click chemistry method,

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has emerged as a unique method to obtain graft and block copolymers. “Click” reactions which are vital for the performance of the materials lead to surface control and functionalization. Lately, “click” techniques have gained importance in the synthesis of new nano-structured polymers and secured their positions in a wide variety of scientific fields. The main characteristics of "click" chemistry are indicated by simple product isolations, high tolerances of functional groups, superior regional selectivity, lack of by-products, light and simple reaction conditions, respectively [37–53].

This study shows the synthesis of poly(ε-caprolactone-b-acryloyl chloride-g-vinyl chloride) [poly(CL-b-AC-g-VC)] ladder-type copolymer by using reversible addition fragmentation chain transfer polymerization (RAFT), ROP and "click" chemistry. Firstly, chain transfer agent (RAFT-ROP agent) was obtained using potassium salt of ethyl xanthogenate and 5-bromo-2-hydroxybenzaldehyde [54]. Secondly, poly(ε-caprolactone-b-acryloyl chloride) [poly(CL-b-AC)] block copolymer was synthesized by using chain transfer agent to initiate polymerization of ε-caprolactone (ε-CL) and acryloyl chloride (AC) in one-step. Then, azido poly(ε-caprolactone-b-acryloyl chloride) (PCL-b-PAC-N_3) block copolymer was obtained through azidation of the poly(CL-b-AC) block copolymers with NaN_3. Thirdly, PVC-propargyl was obtained by reaction of propargyl alcohol and polyvinyl chloride (PVC), as shown in the literature [55]. Lastly, PCL-b-PAC-N_3 and PVC-propargyl were used by "click" chemistry to synthesize poly(CL-b-AC-g-VC) ladder-type copolymer. This work is an example of a type of combination reaction, from ROP and RAFT to "click" chemistry. In addition to this, the papers on the combination polymerization reactions including "click" chemistry appeared recently. For example, from ROP to RAFT [27, 54], and from ROP to "click" chemistry [35, 57]. These methods for synthesis of ladder-type copolymer are simple and efficient. The current study can be a simple example of this point of view. This study provides novel, well-characterized materials with potential industrial application through the synergistic combination of the PCL, PAC and PVC. In this work, we attempt to report the synthesis of the ladder-type copolymer via RAFT, ROP, and "click" chemistry methods. Characterization of the block and ladder-type copolymer were comprehensively fulfilled by ^{1}H-NMR, GPC, FT-IR, SEM, TGA and DSC.

Materials and methods

Chemicals

Propargyl alcohol (99% Aldrich), PVC (approximately Mn = 22,000 $gmol^{-1}$, Sigma-Aldrich), 5-bromo-2-hydroxybenzaldehyde (98% Merck), potassium ethyl xanthogenate (96% Aldrich), N,N,N’,N’,N’’ pentametildietilentriamin (PMDETA) (98% J&K Scientific), Acryloyl chloride (AC) (> 97% Aldrich), Copper(l) bromide (CuBr) (98% J&K Scientific), ε-caprolactone (ε-CL) (97% Sigma-Aldrich), Sodium azide (NaN_3) (99.5% Chemsolute), 2,2′-azobis(2-methylpropionitrile) (AIBN) (99% Aldrich), stannous octoate [$Sn(Oct)_2$] (95% J&K Scientific), Triethylamine (TEA) (≥ 99% Sigma-Aldrich), N,N-dimethylformamide (DMF) (99.9% Chemsolute), methanol (≥ 99.7% Sigma-Aldrich), Diethyl ether (99.5% Riedel–de Haen), Petroleum ether (Riedel–de Haen), Tetrahydrofuran (THF) (≥ 99.0% Honeywell).

Instrumentation

The number average molecular weights (Mn,GPC), the weight average molecular weights (Mw,GPC) and dispersities were examined with HPLC/GPC-Shimadzu RID-10A GPC instrument with tetrahydrofuran mobile phase as the solvent 40 °C using Refractive Index Detector (RID-10A). Mw of polystyrene standarts were Mw values of the polystyrene standards were 1490, 2500, 5480, 9500, 20,800, 53,500, 171,000, 295,900, 410,000, and 566,200 Da. ^{1}H-NMR spectra were detected using Bruker Ultra Shield Plus, ultra-long hold time 400 NMR spectrometer using Dimethyl sulfoxide-d_6 as solvent. FTIR-attenuated total reflectance (FTIR-ATR) were detected using PerkinElmer Frontier Model and Alpha-P Bruker FT-IR spectrometer. Scanning Electron Microscopy (SEM) images were taken on a Carl Zeiss Sigma 300 Field Emission electron microscope were coated with a thin layer of gold on the polymers surfaces. Thermogravimetric analysis (TGA) measurements were conducted using a Seiko II Exstar 6000 model instrument. The samples were heated at a rate of 10 °C/min from 25 °C to 600 °C under N_2 gas. Diferential scanning calorimetry (DSC) measurements were conducted at a rate of 10 °C/min from -80 °C to 150 °C under N_2 atmosphere using a Perkin Elmer DSC 8500 series instrument.

Synthesis of chain transfer agent (RAFT-ROP agent)

RAFT-ROP agent was synthesized as the literature [54]. For example, a 100 mL flask was mixed with 30 mL of THF, 1.504 g of 5-bromo-2-hydroxybenzaldehyde, 3.014 g of potassium ethyl xanthogenate, respectively. The flask containing the mixture was placed on a magnetic stirrer in an oil bath at 30 °C. After 72 h, the content was filtered to remove the unreacted xanthate. Solvent partially removed. The residue was precipitated in (1v/1v) cold diethyl ether and petroleum ether. The produce was kept in a refrigerator

overnight. After decantation, RAFT-ROP agent was dried in a vacuum oven at room temperature for 48 h without solvent. The synthesis amount of the RAFT-ROP agent was determined gravimetrically.

Synthesis of poly(ε-caprolactone-b-acryloyl chloride)[poly(CL-b-AC)] block copolymer

The general procedure for one-step polymerization of poly(CL-b-AC) block copolymeris as follows: to a round bottom 25 mL flask equipped with magnetic stirring bar, 0.101 g of chain transfer agent (RAFT-ROP agent), 5 mL of solvent (DMF),0.080 g of stannous octoate [$Sn(Oct)_2$], 1.503 g of ε-caprolactone (ε-CL), 1.518 g of acryloyl chloride (AC), 0.001 gof 2,2′-azobis(2-methylpropionitrile) (AIBN) were added, respectively. The flask was degassed by flushing pure argon gas and placed in a thermostated silicon-oil bath at 90 °C temperature. The block copolymers formed were precipitated in ten-fold methanol.

Synthesis of terminally azido poly(ε-caprolactone-b-acryloyl chloride) [PCL-b-PAC-N_3] block copolymer

0.450 g of poly(CL-b-AC) block copolymer, 0.206 g of NaN_3, and 5 mL of DMF were added into a round bottom 25 mL flask. The flask was degassed by flushing pure argon gas. The reaction flask was immersed in an oil bath at 35 °C on a magnetic stirrer. After 72 h, the samples were filtered. The solution was drained into excess methanol to separate PCL-b-PAC-N_3. After decantation, obtained product was dried at room temperature under vacuum for 72 h.

Synthesis of polyvinyl chloride propargyl (PVC-propargyl)

The similar procedure reported in the cited literature was used for synthesis of propargyl PVCs by using PVC [55]. For example, 0.501 g of PVC in 5 mL of CH_2Cl_2 was mixed with 2 mL of TEA. The reaction mixture was cooled down to below 0 °C and argon gas was injected into the flask. This solution was added 0.680 g of propargyl alcohol in 3 mL of CH_2Cl_2 via a dropping funnel for the duration of half an hour. The reaction mixture was stirred for two hours at down to below 0 °C. The mixture was stirred at 50 °C for 72 h. The resulting product was precipitated into cold methanol. Afterwards decantation, the samples was dried at 25 °C in a vacuum oven for two days.

Synthesis of poly(ε-caprolactone-b-acryloyl chloride-g-vinyl chloride) [poly(CL-b-AC-g-VC)] ladder-type copolymer by "click" chemistry

Poly(CL-b-AC-g-VC) ladder-type copolymer was synthesized by "click" chemistry. 0.202 g of PCL-b-PAC-N_3 blok copolymer and 0.403 g of PVC-propargyl were dissolved in argon purged 4 mL of DMF in schlenk tube. 0.020 mL of PMDETA and 0.014 g of CuBr were added in the schlenk tube followed by injecting argon for 5 min and then the tube was placed in an oil bath at 30 °C on a magnetic stirrer. Then 72 h, the tube content was filtered. The sample was drained into cold methanol to separate precipitated poly(CL-b-AC-g-VC) ladder-type copolymer. After decantation, the copolymer was dried in a vacuum oven at 25 °C.

Results and discussion

Synthesis of RAFT-ROP agent

First of all, chain transfer agent (RAFT-ROP agent) was obtained by reaction of 5-bromo-2 hydroxybenzaldehyde and potassium ethyl xanthogenate as a light brown solid. The yield was obtained with a 36.1 wt %. The synthesized chain transfer agent was characterized by using FT-IR and ^{1}H-NMR. FT-IR spectrum of RAFT-ROP agentin Fig. 1 shows the signals at 3300 cm^{-1} for -OH group, 2973–2865 cm^{-1} for -CH and CH_3 group, 1640 cm^{-1} for -C = O group, 1132 cm^{-1} for -COC group, 1087 cm^{-1} for -SC group. The ^{1}H-NMR spectrum of RAFT-ROP agentin Fig. 2 displayed peaks at; (δ, ppm): 7.84 (b, –HC = O), 7.03 (c, aromatic -CH), 4.65 (d, CH_2), 4.02 (a, OH), 1.48 (e, CH_3). The chemical synthesis mechanism of RAFT-ROP agent was shown in Scheme 1(first line).

Synthesis of poly(CL-b-AC) block copolymer

Poly(CL-b-AC) block copolymerwas synthesized by the combination of RAFT and ROP in one-step in the presence of ε-CL, AC and chain transfer agent (RAFT-ROP agent) with $Sn(Oct)_2$ as a catalyst. The yield was found as 56.43 wt %. The block copolymer was characterized ^{1}H-NMR, FT-IR, SEM and TGA measurements. FT-IR spectrum of poly(CL-b-AC) block copolymer in Fig. 3a shows the signals about 2950–2865 cm^{-1} for -CH and CH_2 group, 1721 cm^{-1} for -C = O group, 1170 cm^{-1} for -COC group, 1107 cm^{-1} for -SC group. The ^{1}H-NMR spectrum of poly(CL-b-AC) block copolymer in Fig. 4a displayed peaks at; (δ, ppm):

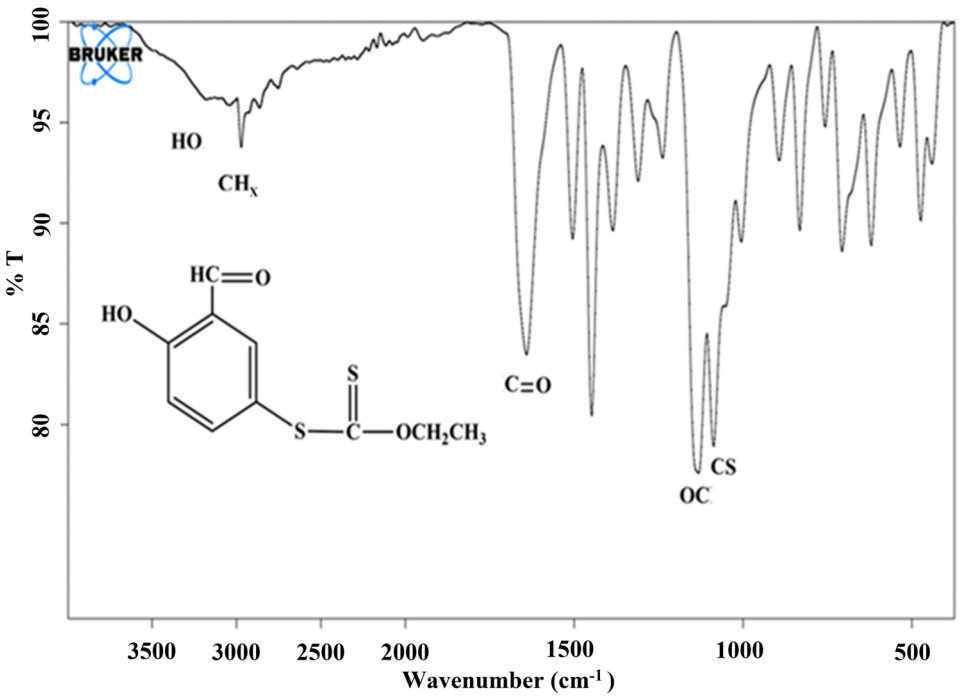


Fig. 1 FT-IR spectrum of the chain transfer agent (RAFT-ROP agent)

4.00 (e, CH_3O of ethyl xanthogenate unit, d, CH_3O of PCL unit), 3.58 (ı, OH of PCL unit), 3.40 (f, CH of PAC unit), 2.50 (c, CH_2CO of PCL unit), 2.28 (g, CH_2 of PAC unit), 1.55(b, CH_2 of PCL unit), 1.30 (a, CH_2 of PCL unit) 1.15 (h, CH_3 of ethyl xanthogenate unit). Scheme 1 (second line) shows the synthesis path for the block copolymer.

Synthesis of PCL-b-PAC-N_3 block copolymer

Scheme 1 (third line) shows the reaction pathway for PCL-b-PAC-N_3. The yield was 0.441 g. The gravimetric yield obtained from the weight of PCL-b-PAC-N_3 was 67.20 wt%. PCL-b-PAC-N_3 was characterized ^{1}H-NMR, FT-IR and GPC measurements. FT-IR spectrum

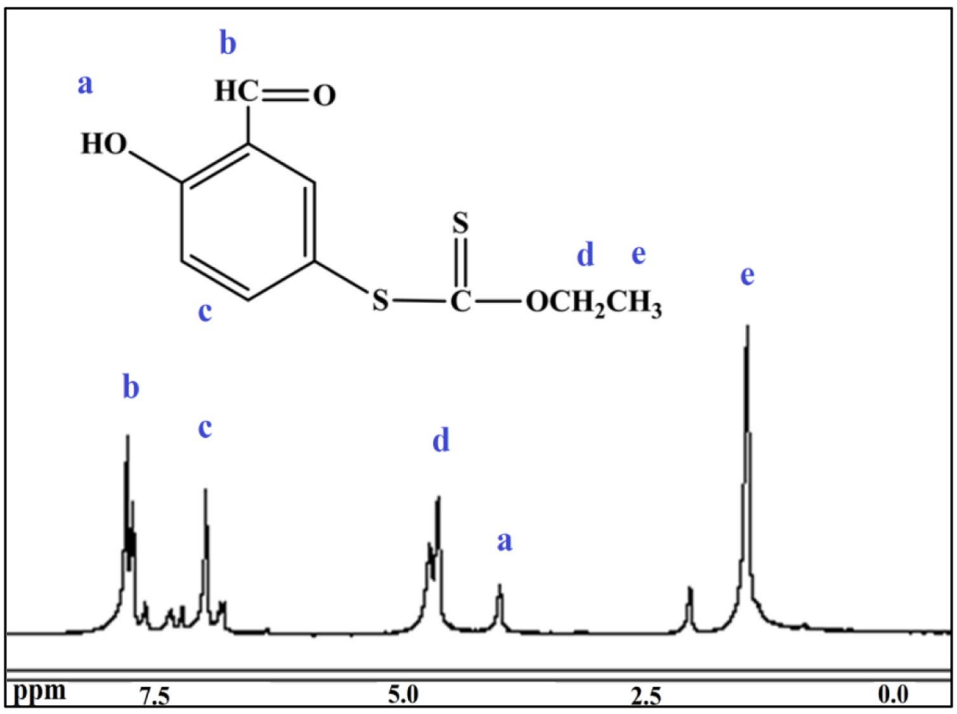
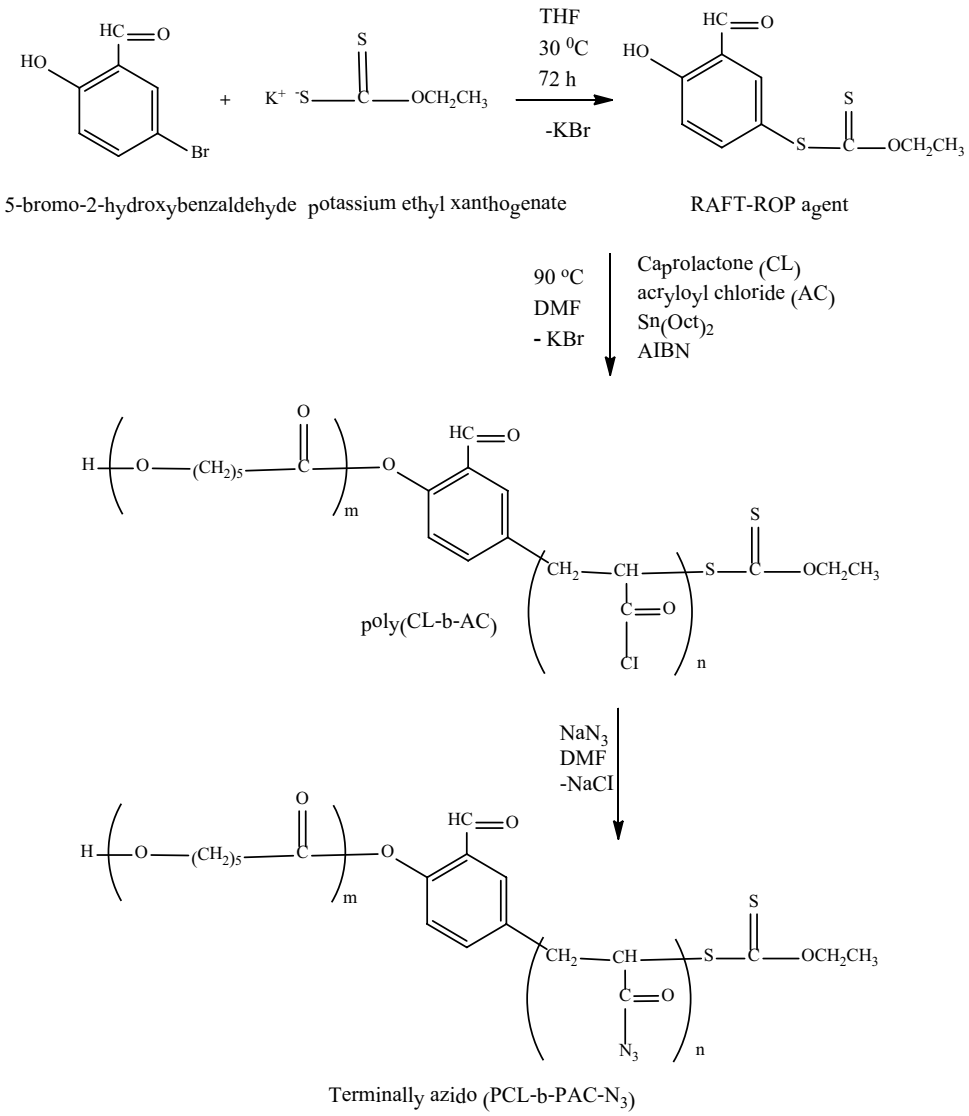


Fig. 2 ^{1}H-NMR spectrum of the chain transfer agent (RAFT-ROP agent)

Scheme 1 Reaction outlines for syntheses of RAFT-ROP agent, poly(CL-b-AC) block copolymer and PCL-b-PAC-N_3 block copolymer



of PCL-b-PAC-N_3 in Fig. 3b shows the signals about 2950–2865 cm^{-1} for -CH and CH_2 group, 2095 for cm^{-1} N_3 group, 1720 cm^{-1} for -C = O group,1174 cm^{-1} for -COC group, 1107 cm^{-1} for -SC group. Figure 3b for FT-IR spectrum of PCL-b-PAC-N_3 block copolymer shows small band feature at about 2095 cm^{-1} specific for stretching vibration of azide. This was an important proof for azidation of PCL-b-PAC block copolymer. Namely, creation of specific -N_3 stretching band at about 2095 cm^{-1} shows effective azidiation of PCL-b-PAC block copolymer. The ^{1}H-NMR spectrum of PCL-b-PAC-N_3 in Fig. 4b displayed peaks at; (δ, ppm): 4.00 (e, CH_3O of ethyl xanthogenate unit, d, CH_3O of PCL unit), 3.58 (ı, OH of PCL unit), 3.36 (f, CH of PAC unit), 3.32 (DMSO), 2.50 (c, CH_2CO of PCL unit), 2.28 (g, CH_2 of PAC unit), 1.53 (b, CH_2 of PCL unit), 1.29 (a, CH_2 of PCL unit), 1.15 (h, CH_3 of ethyl xanthogenate unit). Mn value of PCL-b-PAC-N_3 block copolymer was obtained 4,534 g.mol^{-1}. Dispersity value of PCL-b-PAC-N_3 block copolymer was found to be 1.31. GPC trace of the block copolymer was given as supplementary data.

Synthesis of PVC-propargyl

PVC-propargyl was synthesized by reacting PVC and propargyl alcohol. The gravimetric yield obtained from the weight of PVC-propargyl was 56.09 wt%. Scheme 2 (first line) includes the reaction pathway for the synthesis of PVC-propargyl. FT-IR spectrum of PVC-propargyl in Fig. 3c shows the signals at 3220 cm^{-1} for C≡C group, 2980 cm^{-1} for aliphatic -CH and CH_2 group, and 1254 cm^{-1} for -COC group. The formation of the C≡C band at about 3220 cm^{-1} proves the successful propargylation of PVC. The ^{1}H-NMR spectrum of PVC-propargyl in Fig. 4c displayed peaks at; (δ, ppm): 4.50 (t,

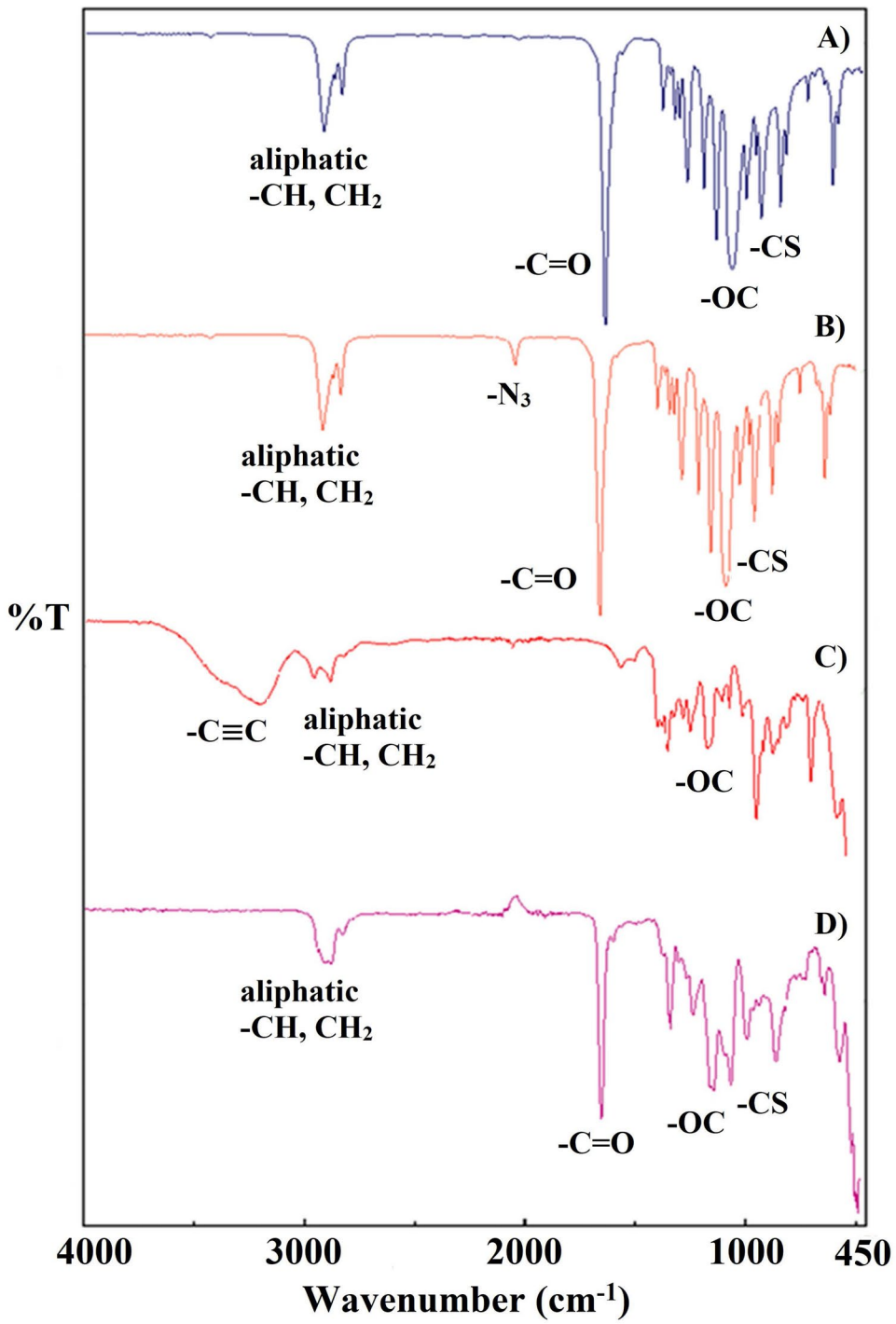


Fig. 3 FT-IR spectra of (**a**) poly(CL-b-AC) block copolymer; (**b**) PCL-b-PAC-N_3 block copolymer; (**c**) PVC-propargyl; (**d**) poly(CL-b-AC-g-VC) ladder-type copolymer

CH), 4.00 (v, CHO) 3.40 (DMSO), 3.26 (y,CH_2O), 2.50 (s, CH_2), 1.25 (x, C≡CH). Mn value of PVC-propargyl was obtained 34,163 g.mol^{-1} and dispersity of PVC-propargyl was 2.11. GPC trace of PVC-propargyl was given as supplementary data.

Synthesis of poly(CL-b-AC-g-VC) ladder-type copolymerby "click" chemistry

Poly(CL-b-AC-g-VC) ladder-type copolymerwas reported by means of "click"chemistry, RAFT and ROP methods. These

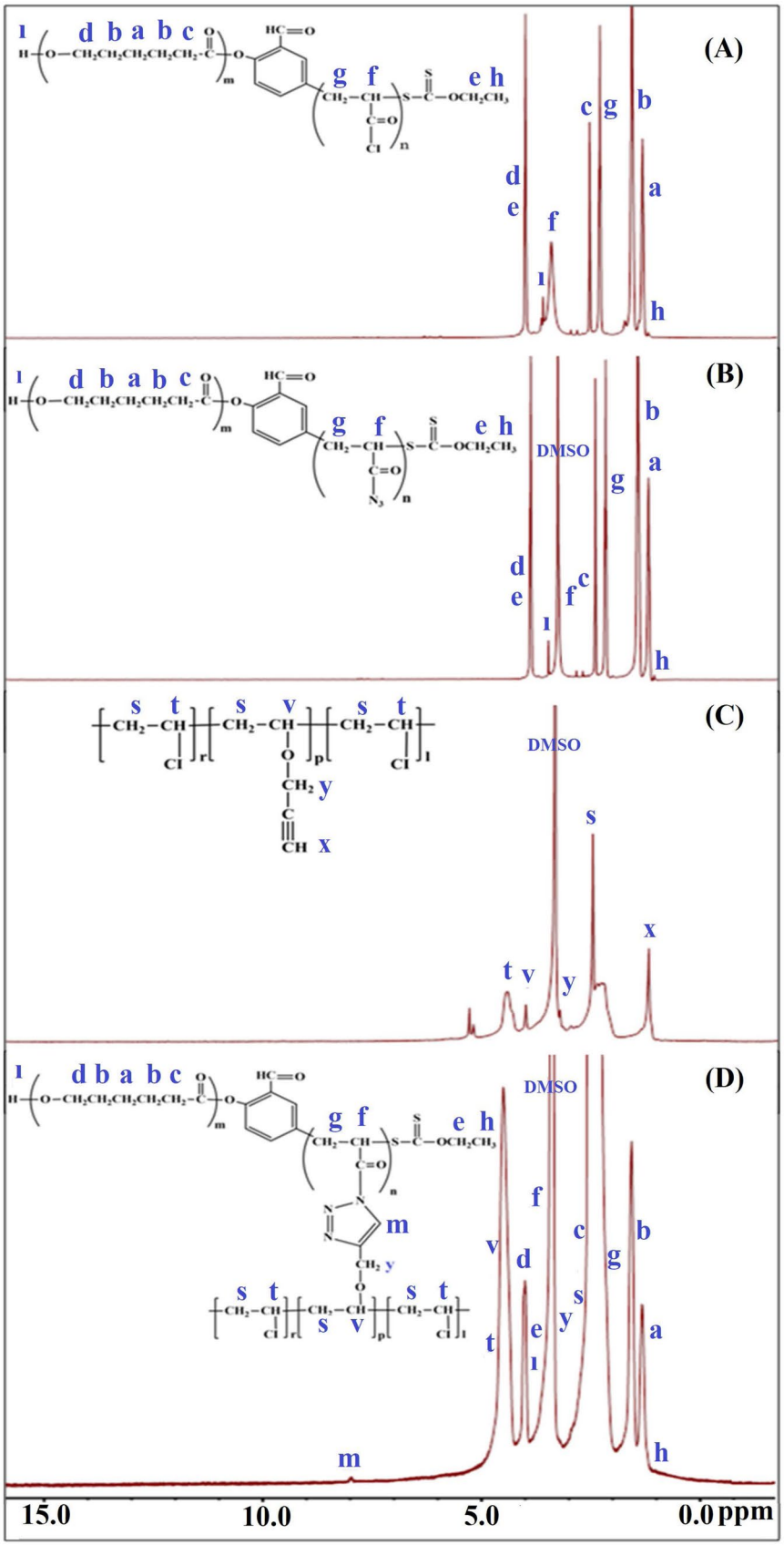
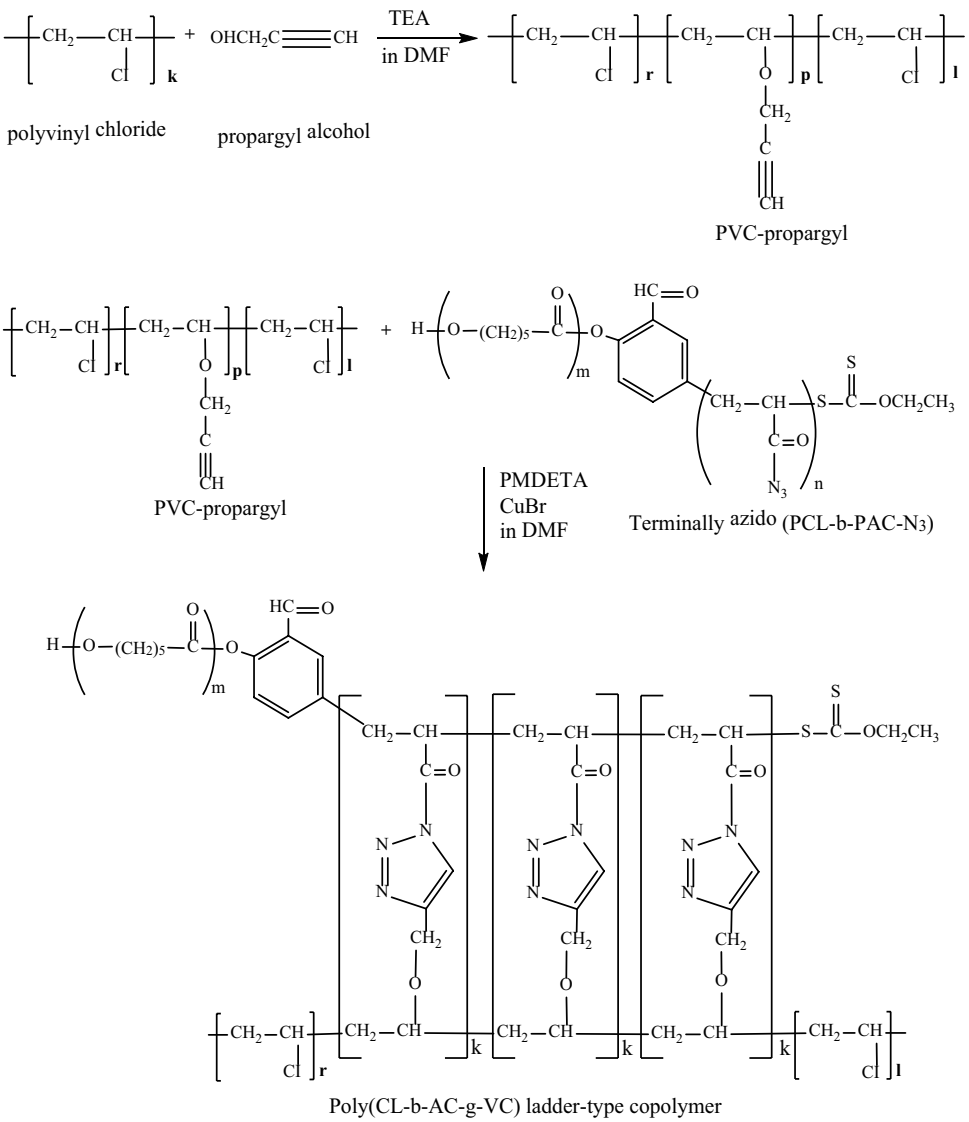


Fig. 4 ^{1}H-NMR spectra of (**a**) poly(CL-b-AC) block copolymer; (**b**) PCL-b-PAC-N_3 block copolymer; (**c**) PVC-propargyl; (**d**) poly(CL-b-AC-g-VC) ladder-type copolymer

methods used for polymer synthesis is simple, effective, environmentally friendly and has low energy consumption. The yield of poly(CL-b-AC-g-VC) ladder-type was 72.40 wt%. FT-IR spectrum of poly(CL-b-AC-g-VC) ladder-type copolymer in Fig. 3d shows the signals at about 2950–2850 cm^{-1} for -CH and CH_2 group, 1726 cm^{-1} for -C=O group, 1239 cm^{-1} for -COC group. FT-IR spectrum of poly(CL-b-AC-g-VC) ladder-type copolymer, disappearance of specific $-N_3$ stretching band shows to obtain poly(CL-b-AC-g-VC) ladder-type copolymer. The ^{1}H-NMR spectrum of poly(CL-b-AC-g-VC) ladder-type copolymer in Fig. 4d displayed peaks at; (δ, ppm):7.95 (m, CH of triazole),4.50 (t, CH of PVC unit), 4.30 (v, CHO of PVC unit) 4.00 (d, CH_3O of PCL unit), 3.90 (ı, OH of PCL unit), 3.42(f, CH of PAC unit), 3.36 (d-DMSO), 2.50 (c, CH_2CO of PCL unit, s, CH_2 of PVC unit), 2.28 (g, CH_2 of PAC unit), 1.58 (b, CH_2 of PCL unit), 1.32 (a, CH_2 of PCL unit).The CH protons of the triazole ring acting as a bridge were seen at about 7.95 ppm and this is evidence that the polymerization has been successful. The secondline in Scheme 2 contains the basicoutline for the synthesis of poly(CL-b-AC-g-VC) ladder-type copolymer. Mn value of poly(CL-b-AC-g-VC) ladder-type copolymer was 55,378 $g.mol^{-1}$. Dispersity value of the ladder-type copolymer formed by "click" reaction was found to be 1.38. Increases in the molecular weight of the ladder-type copolymer as compared with these of reactants is consistent with the formation of the copolymer.

Thermal analysis of poly(CL-b-AC-g-VC) ladder-type copolymer were carried out by DSC and TGA curves. Tg value of the ladder-type copolymerswas 38 °C (Fig. 5). Tg values were reported in the literature for homo PCL and homo PVC as -72 °C [56] and 80 °C [8], respectively. Tg value of the ladder-type copolymers changed to the value which was less than the value of PVC because of PCL



Scheme 2 Reaction pathways in the syntheses of PVC-propargyl and poly(CL-b-AC-g-VC) ladder-type copolymer

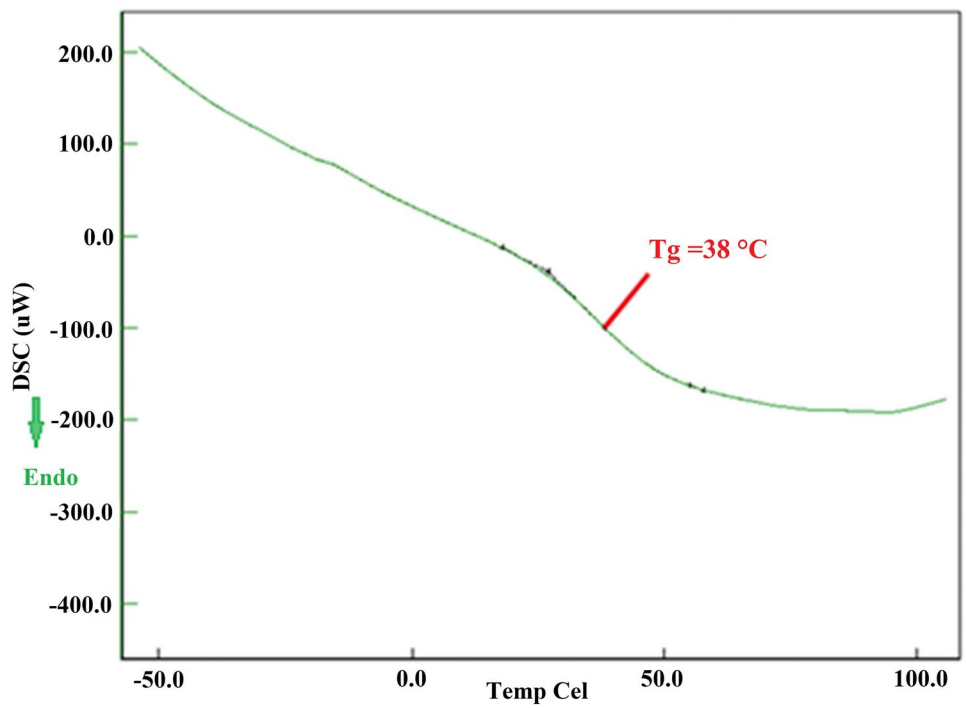


Fig. 5 DSC curve of poly(CL-b-AC-g-VC) ladder-type copolymer

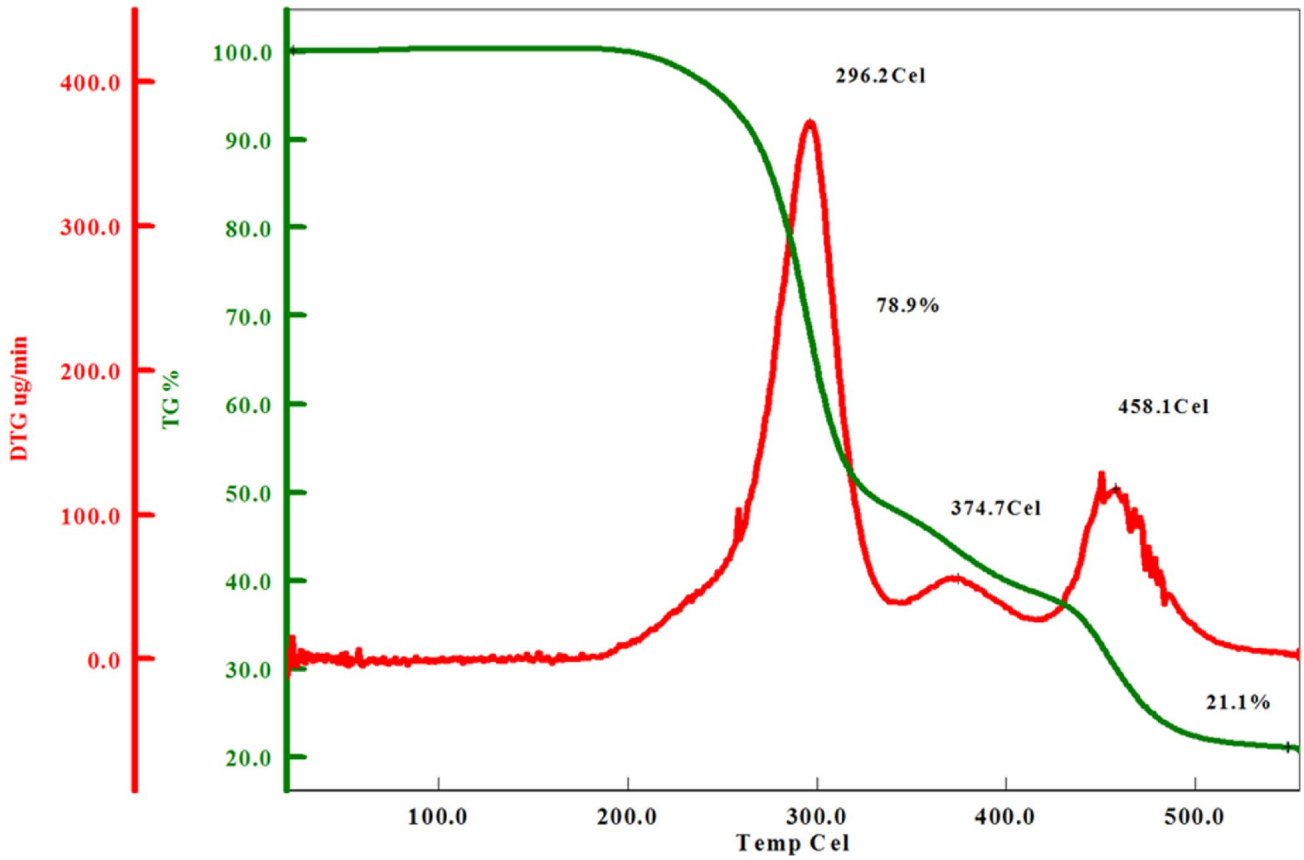


Fig. 6 TGA curve of poly(CL-b-AC-g-VC) ladder-type copolymers

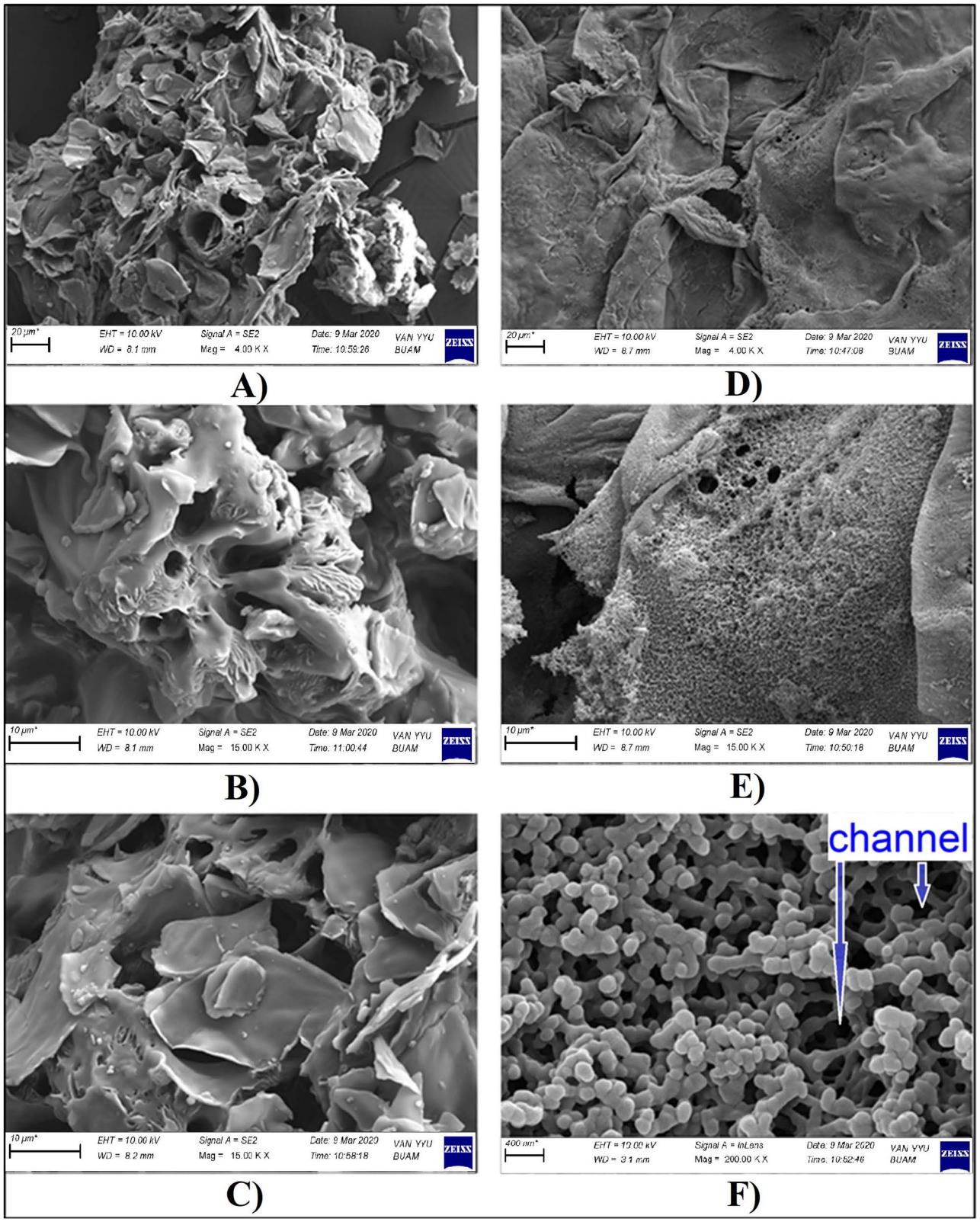


Fig. 7 SEM images of poly(CL-b-AC) block copolymer; 4000 X (**A**), 15,000 X (**B**), 15,000 X (**C**) and poly(CL-b-AC-g-VC) ladder-type copolymer; 4000 X (**D**), 15,000 X (**E**), 200,000 X (**F**)

segment. The only one glass transition temperature value for the poly(CL-b-AC-g-VC) ladder-type copolymer shows the miscible nature of the related polymers. Tg value of the ladder-type copolymers was consistent with theoretical Tg values of the homopolymers. Decomposition temperature (Td) of poly(CL-b-AC-g-VC) ladder-type copolymer obtained from TGA. TGA curve of poly(CL-b-AC-g-VC) ladder-type copolymer has showed interesting properties of the copolymers indicating continuous weight loss starting from 180 °C to nearly 550 °C with derivatives at 296 °C, 375 °C and 458 °C through three steps (Fig. 6).

To examine the morphological properties of poly(CL-b-AC) block copolymer and poly(CL-b-AC-g-VC) ladder-type copolymers, SEM was used. The surface morphologies poly(CL-b-AC) block copolymer and poly(CL-b-AC-g-VC) ladder-type copolymerwas shown in Fig. 7. According to the SEM images of poly(CL-b-AC) block copolymer has ivy and strongly intermingles structure. According to the SEM images of poly(CL-b-AC-g-VC) ladder-type copolymers, homogenization of the copolymer was good. The copolymer samples were characterized by a morphology consisting platelets with channels. The SEM images of the ladder-type copolymers show a rough surface and form a continuous phase.

Conclusions

In this study, the synthesis of ladder-type copolymer with the combination of many polymer synthesis techniques ("click"chemistry, RAFT, ROP) was studied. These methods used for polymer syntheses are simple, effective, environmentally friendly and have low energy consumption. In addition to allowing polymer synthesis with different architecture by using different monomers with the click reaction, the superior properties of the triazole ring formed as a result of the click reaction have been utilized. These methods are simple and effective for synthesizing the ladder-type copolymers. The characterization of the products was accomplished by using FT-IR, ^{1}H-NMR, SEM, TGA, DSC and GPC analyses.

References

1. Gacal B, Cianga L, Agag T, Takeichi T, Yagci Y (2007) Synthesis and characterization of maleimide (Co) polymers with pendant benzoxazine groups by photoinduced radical polymerization and their thermal curing. J Polym Sci Part A: Polym Chem 45(13):2774–2786. https://doi.org/10.1002/pola.22034
2. Şanal T, Koçak İ, Hazer B (2017) Synthesis of comb-typeamphiphilic graft copolymers derived from chlorinated poly(ε-caprolactone) via click reaction. Polym Bull 74:977–995. https://doi.org/10.1007/s00289-016-1757-5
3. Savaş B (2015) Synthesis of macro monomers containing triazol ring and graft polymerization (Triazol halkası ihtiva eden makromonomerlerin sentezi ve graft kopolimerizasyonu) PhD Thesis Kafkas University Kars Turkey
4. Bolton J, Rzayev J (2012) Tandem RAFT-ATRP synthesis of polystyrene–poly(methyl methacrylate) bottle brush block copolymers and their self-assembly into cylindrical nanostructures. ACS Macro Lett 1:15–18. https://doi.org/10.1021/mz200003j
5. Kwon GS, Kataoka K (2012) Block copolymer micelles as long-circulating drug vehicles. Adv Drug Deliv Rev 64:237–245. https://doi.org/10.1016/j.addr.2012.09.016
6. Öztürk T, Savaş B, Meyvacı E, Kılıçlıoğlu A, Hazer B (2020) Synthesis and characterization of the block copolymers using the novel bifunctional initiator by RAFT and FRP technics: evaluation of the primary polymerization parameters. J Polym Res 27(3):1–7. https://doi.org/10.1007/s10965-020-2043-7
7. Çatıker E, Öztürk T, Atakay M, Salih B (2020) Synthesis and characterization of the ABA-type poly(ester-ether-ester) block copolymers. J Macromol Sci 57:600–609. https://doi.org/10.1080/10601325.2020.1745080
8. Öztürk T, Göktaş M, Savaş B, Işıklar M, Atalar MN, Hazer B (2014) Synthesis and characterization of poly (vinyl chloride-graft-2-vinylpyridine) graft copolymers using a novel macroinitiator by reversible addition-fragmentation chain transfer polymerization. e-Polymers 14(1):27–34. https://doi.org/10.1515/epoly-2013-0011
9. Tunca U, Karlıga B, Ertekin S, Ugur AL, Sirkecioglu O, Hizal G (2001) Synthesis of asymmetric difunctional initiators and their use in the preparation of block copolymers via ATRP and SFRP. Polymer 42:8489–8493. https://doi.org/10.1016/S0032-3861(01)00235-X
10. Dizman C, Kahveci MU, Yagci Y (2013) Synthesis of polysulfoneb-polystyrene block copolymers by mechanistic transformation from condensation polymerization to free radical polymerization. Polym Bull 70:2097–2109. https://doi.org/10.1007/s00289-013-0931-2
11. Teo YC, Lai HW, Xia Y (2017) Frontispiece: Synthesis of ladder polymers: developments, challenges, and opportunities. Chem Eur J 23(57). https://doi.org/10.1002/chem.201785761
12. Schlüter AD (1991) Ladder polymers: the new generation. Adv Mater 3 (6): 282–291. https://doi.org/10.1002/adma.19910030603
13. Lee J, Kalin AJ, Wang C, Early JT, Al-Hashimi M, Fang L (2018) Donor–acceptor conjugated ladder polymer via aromatization-driven thermodynamic annulation. Polym Chem 9(13):1603–1609. https://doi.org/10.1039/C7PY02059G
14. Erdogan T, Gungor E, Durmaz H, Hizal G, Tunca U (2006) Photoresponsive poly (methylmethacrylate) 2–(polystyrene) 2 miktoarm star copolymer containing an azobenzene moiety at the core. J Polym Sci Part A-1: Polym Chem 44(4):1396–1403. https://doi.org/10.1002/pola.21253
15. Kawahara N, Kojoh S, Matsuo S, Kaneko H, Matsugi T, Saito J, Kashiwa N (2006) Synthetic method of polyethylenepoly(methylmethacrylate) (PE-PMMA) polymer hybrid via reversible addition-fragmentation chain transfer (RAFT) polymerization with functionalized polyethylene. Polym Bull 57:805–812. https://doi.org/10.1007/s00289-006-0642-z
16. Göktaş M, Olgun B (2019) One-step synthesis and characterization of poly (ε-caprolactone)-b-poly (N-isopropylacrylamide) thermo-responsive block copolymers via RAFT and ROP techniques. Polym Sci Series B 61(4):421–429. https://doi.org/10.1134/S1560090419040055
17. Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, Mayadunne RTA, Meijs GF, Moad CL, Moad E, Rizzardo E, Thang SH (1998) Livingfree-radical polymerization by reversible

addition-fragmentation chain transfer: the RAFT process. Macromolecules 31:5559–5562. https://doi.org/10.1021/ma9804951
18. Öztürk T, Hazer B (2010) Synthesis and characterization of a novel macromonomer initiator for reversible addition fragmentation chain transfer (RAFT). Evaluation of the polymerization kinetics and gelation behaviors. J Macromol Sci Part A Pure Appl Chem 47:265–272. https://doi.org/10.1080/10601320903527095
19. Göktaş M (2020) Synthesis and characterization of temperature-responsive block copolymers using macromonomeric initiator. Chem Pap 1–11. https://doi.org/10.1007/s11696-020-01074-9
20. Muñoz-Lópe CN, Díaz-Silvestre S, Telles-Padilla JG, Rivera Vallejo C, St Thomas C, Jiménez-Regalado E (2019) Synthesis, characterization and rheological properties of multi-block associative copolymers by RAFT technique. Polym Bull 2019. https://doi.org/10.1007/s00289-019-02867-z
21. Hazer B, Arslan H, Senemoğlu Y, Şen Ş (2019) Synthesis of block/ graft copolymers based on vinyl benzyl chloride via reversible addition fragmentation chain transfer (raft) polymerization using the carboxylic acid functionalized trithiocarbonate. J Polym Res 26:101. https://doi.org/10.1007/s10965-019-1763-z
22. Öztürk T, Atalar MN, Göktaş M, Hazer B (2013) One-step synthesis of block-graft copolymers via simultaneous reversible-addition fragmentation chain transfer and ring-opening polymerization using a novel macroinitiator. J Polym Sci A Polym Chem 51:2651–2659. https://doi.org/10.1002/pola.26654
23. Yıldıko Ü, Çakmak İ, Öztürk T, Yörük A (2017) Synthesis of poly [ε-caprolacton-b-epichlorohydryin-b-ε-caprolactone]-g-poly(styrene) Block-Graft Copolymers via Cationic Ring Opening and Atom Transfer Radical Polymerization Transformations. Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi 7(3):161–169. https://doi.org/10.21597/jist.2017.174
24. Şanal T, Oruç O, Öztürk T, Hazer B (2015) Synthesis of pH- and thermo-responsive poly(ε-caprolactone-b-4-vinyl benzyl-gdimethyl amino ethyl methacrylate) brush type graft copolymers via RAFT polymerization. J Polym Res 22:1–12. https://doi.org/10.1007/s10965-014-0640-z
25. Montoya-Villegas KA, Licea-Claveríe Á, Zapata-González I, Gómez E, Ramírez-Jiménez A (2019) The effect in the RAFT polymerization of two oligo(ethylene glycol) methacrylates when the CTA 4-cyano-4-(propylthiocarbonothioylthio) pentanoic acid is auto-hydrolyzed to its corresponding amide. J Polym Res 26:71. https://doi.org/10.1007/s10965-019-1718-4
26. Liu C, Ren X (2018) Synthesis and characterization of controlled benzotriazole light stabilizer by RAFT polymerization and its application. J Polym Res 25:97. https://doi.org/10.1007/s10965-018-1491-9
27. Öztürk T, Kayğın O, Göktaş M, Hazer B (2016) Synthesis and characterization of graft copolymers based on polyepichlorohydrin via reversible addition-fragmentation chain transfer polymerization. J Macromol Sci Part A Pure Appl Chem 53:362–367. https://doi.org/10.1080/10601325.2016.1166002
28. Liu S, Tian L, Mao H, Ning W, Shang P, Wu J, Shi X (2018) Micellization and sol-gel transition of novel thermo- and pHresponsive ABC tribl°Ck copolymer synthesized by RAFT. J Polym Res 25:264. https://doi.org/10.1007/s10965-018-1658-4
29. Öztürk T, Göktaş M, Hazer B (2010) Synthesis and characterization of poly(methyl methacrylate-block-ethylene glycol-block-methyl methacrylate) block copolymers by reversible addition fragmentation chain transfer polymerization. J Macromol Sci Part A Pure Appl Chem 48:65–70. https://doi.org/10.1080/10601325.2011.528310
30. Coulembier O, Degee P, Hedrick JL, Dubois P (2006) From controlled ring-opening polymerization to biodegradable aliphatic polyester: Especially poly (β-malic acid) derivatives. Prog Polym Sci 31:723–747. https://doi.org/10.1016/j.progpolymsci.2006.08.004
31. Deanin RD (1992) New useful polymers by Ring-Opening Polymerization. Polym Plast Technol 31:229–239. https://doi.org/10.1080/03602559208017745
32. Charoongchit P, Suksiriworapong J, Sripha K, Mao S, Sapin-Minet A, Maincent P, Junyaprasert VB (2017) Self-aggregation of cationically modified poly (ε-caprolactone) 2-co-poly (ethylene glycol) copolymers: Effect of cationic grafting ligand and poly (ε-caprolactone) chain length. Mater Sci Eng C Mater Biol Appl 72:444–445. https://doi.org/10.1016/j.msec.2016.11.043
33. Öztürk T, Meyvacı E (2017) Synthesis and characterization poly(ε-caprolactone-b-ethylene glycol-b-ε-caprolactone) ABA type block copolymersvia "click" chemistry and ring-opening polymerization. J Macromol Sci A Pure Appl Chem 54(9):575–581. https://doi.org/10.1080/10601325.2017.1309251
34. Tian LL, Wu BB, Wang ZX (2017) Crown ether complexes of sodium and potassium 2-(benzotriazol-2-yl)phenolates: synthesis and catalysis towards the Ring-Opening Polymerization of Raclactide. J Macromol Sci Part A: Pure and Appl 54:944-950. https://doi.org/10.1080/10601325.2017.1381925
35. Öztürk T, Kılıçlıoğlu A, Savaş B, Hazer B (2018) Synthesis and characterization of poly(ε-caprolactone-co-ethylene glycol) star-type amphiphilic copolymers by "click" chemistry and ring-opening polymerization. J Macromol Sci Part A. https://doi.org/10.1080/10601325.2018.1481344
36. Degirmenci M, Hizal G, Yagci Y (2002) Synthesis and characterization of macrophotoinitiators of poly(e-caprolactone) and theiruse in block copolymerization. Macromolecules 35:8265–8270. https://doi.org/10.1021/ma020668t
37. Balasubramanian R, Kumutha K (2016) Sarojadevi M Mechanical, thermal and electrical properties of polyimides containing 1, 2, 3-triazole ring prepared by click reaction. Polym Bull 73:309–330. https://doi.org/10.1007/s00289-015-1488-z
38. Moses JE, Moorhouse AD (2007) The growing applications of click chemistry. Chem Soc Rev 36:1249–1262. https://doi.org/10.1039/B613014N
39. Kolb HC, Finn MG, Sharpless KB (2001) Click chemistry: diverse chemical function from a few good reactions. Angew Chem Int Edit 40:2004–2021. https://doi.org/10.1002/15213773(20010601)40:11%3c2004:AIDANIE2004%3e3.0.CO;2–5
40. Binder WH, Sachsenhofer R (2007) 'Click' chemistry in polymer and materials science. Macromol Rapid Commun 28:15–54. https://doi.org/10.1002/marc.200600625
41. Hein CD, Liu XM, Wang D (2008) Click chemistry, a powerful tool for pharmaceutical sciences. Pharm Res 25:2216–2230. https://doi.org/10.1007/s11095-008-9616-1
42. Zhu DY, Cao GS, Qiu WL, Rong MZ, Zhang MQ (2015) Self-healing polyvinyl chloride (PVC) based on microencapsulated nucleophilic thiol-click chemistry. Polymer 69:1–9. https://doi.org/10.1016/j.polymer.2015.05.052
43. Öztürk T, Cavicchi CA (2018) Synthesis and characterization of poly(epichlorohydrin-g-ε-caprolactone) graft copolymers by click chemistry. J Polym Mater 35:209–220. https://doi.org/10.32381/JPM.2018.35.02.6
44. Savaş B, Öztürk T, Meyvacı E, Hazer B (2020) Synthesis and characterization of comb-type graft copolymers by redox polymerization and" click" chemistry method. SN Applied Sciences 2(2):181. https://doi.org/10.1007/s42452-020-1985-z
45. Çatıker E, Meyvacı E, Atakay M, Salih B, Öztürk T (2019) Synthesis and characterization of amphiphilic triblock copolymers including β-alanine/α-methyl-β-alanine and ethylene glycol by "click" chemistry. Polym Bull 76:2113–2128. https://doi.org/10.1007/s00289-018-2561-1
46. Asan N, Öztürk T (2017) Synthesis and Characterization of Poly(vinyl chloride–graft–ethylene glycol) Graft Copolymers by "Click" Chemistry. Hacettepe Journal of Biology and Chemistry 45(1):35–42. https://doi.org/10.15671/HJBC.2017.139
47. Öztürk T, Yörümez C (2019) Synthesis of block copolymer including polyepichlorohydrin and polyethylene glycol by "click" chemistry: evaluation of primary parameters of

copolymerization. Polymer Bulletin 1–16. https://doi.org/10.1007/s00289-019-02989-4
48. Xue Y, Ma D, Zhang T, Lin S, Shao S, Gu N (2014) Synthesis and characterization of comb-like methoxy polyethylene glycol-grafted polyurethanes via 'click' chemistry. J Macromol Sci Part A: Pure and Appl Chem 51:456–464. https://doi.org/10.1080/10601325.2014.893145
49. Öztürk T, Meyvacı E, Bektaş H, Menteşe E (2019) Synthesis and characterization of ring-type and branched polymers including polyethylene glycols by "click" chemistry. SN Applied Sciences 1:343. https://doi.org/10.1007/s42452-019-0360-4
50. Xie M, Dang J, Han H, Wang W, Liu J, He X, Zhang Y (2008) Well-defined brush copolymers with high grafting density of amphiphilic side chains by combination of ROP, ROMP and ATRP. Macromolecules 41:9004–9010. https://doi.org/10.1021/ma801408s
51. Kiskan B, Demiray G, Yagci Y (2008) Thermallycurablepolyvinylchloride via click chemistry. J Polym Sci Part A: Polym Chem 46:3512–3518. https://doi.org/10.1002/pola.22685
52. Pawlak M, Grygolowicz-Pawlak E, Crespo GA, Mistlberger G, Bakker E (2013) PVC-based ion-selective electrodes with enhanced biocompatibility by surface modification with "click" chemistry. Electroanalysis 25:1840–1846. https://doi.org/10.1002/elan.201300212
53. Savaş B, Öztürk T (2020) Synthesis and characterization of poly (vinyl chloride-g-methyl methacrylate) graft copolymer by redox polymerization and Cu catalyzed azide-alkyne cycloaddition reaction. J Macromol Sci A 1–7. https://doi.org/10.1080/10601325.2020.1788393
54. Savaş B, Öztürk T (2020) Synthesis and characterization of poly(ε-caprolactone-b-Styrene) block copolymer by ring opening polymerization and reversible addition-fragmentation chain transfer polymerization. Int J Sci Technol 10(3):1759–1766. https://doi.org/10.21597/jist.686682
55. Öztürk T, Meyvacı E, Arslan T (2019) Synthesis and Characterization of Poly(Vinyl Chloride-g-ε-Caprolactone) brush type graft copolymers by ring-opening polymerization and "click" chemistry". J Macromol Sci A Pure Appl Chem 1–10. https://doi.org/10.1080/10601325.2019.1680253
56. Savaş B, Çatıker E, Öztürk T, Meyvacı E (2021) Synthesis and characterization of poly(α-methyl β-alanine)-poly(ε-caprolactone) tri arm star polymer by hydrogen transfer polymerization, ring-opening polymerization and "click" chemistry". J Polym Res 28(2):1–10. https://doi.org/10.1007/s10965-020-02367-z
57. Shuster M, Narkis M, Siegmann A (1994) Polymeric antiplasticization of polycarbonate with polycaprolactone. Polym Eng Sci 34(21):1613–1618. https://doi.org/10.1002/pen.760342106