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Research paper

Modification of the Physical and Thermal Properties of Glycidyl Azide Polymer Through the Formation of a Star-Shaped Polymer

Asghar Bodaghi

Department of Chemistry, Faculty of Science, Qom University,

PO Box: 3716146611, Alghadir Blv. Qom, Iran

E-mail: a.bodaghi1347@gmail.com

ORCID information

<https://orcid.org/0000-0002-0302-8733>

Abstract: Glycidyl azide polymer (GAP) is one of the most important binders in the preparation of propellants. One of the most important problems with this binder is its high glass transition temperature. In the present study, the physical and thermal properties of GAP were modified by the synthesis of a star shaped polymer. Dibromo end-functionalized two-arm polycaprolactone (PCL), $(PCL)_2-(Br)_2$, was synthesized by ring-opening polymerization (ROP) of ϵ -caprolactone monomer using 2,2-bis(bromomethyl)-1,3-propane diol as the initiator and stannous 2-ethylhexanoate as the catalyst. The bromines of the polymer were then replaced by azide groups by reaction with sodium azide (NaN_3). The $(PCL)_2-(Br)_2$ was reacted with propargyl terminated polyepichlorohydrin (PTPECH) *via* a click reaction. Finally, $(PCL)_2-(PTPECH)_2$ was converted into $(PCL)_2-(GAP)_2$ by reaction with NaN_3 . 1H NMR, FT-IR and GPC studies revealed that $(PCL)_2-(GAP)_2$ was obtained. The thermal behaviour of this star polymer was investigated by thermogravimetric analysis (TGA) and derivative thermogravimetry. The results showed that $(PCL)_2-(GAP)_2$ decomposed in two stages. The first stage is related to degradation of the azide groups and the second stage was attributed to degradation of the PCL groups.

Keywords: ring-opening polymerization, click chemistry, glycidyl azide polymer, poly(ϵ -caprolactone), star-polymers

1 Introduction

The synthesis of star-shaped polymers has attracted considerable attention, because they show remarkable properties (having a solid-state, smaller hydrodynamic volume, and lower solution and melt viscosities) compared to those with the same molecular weight and composition. Star-shaped polymers consist of three or more arms connected to a single point or to a central core [1-5]. One of the type of star-shaped polymer is the miktoarm star-shaped polymer [6]. The miktoarm star-shaped polymers (sometimes called asymmetric star polymers, or heteroarm star polymers) consist of two or more arms with different chemical composition, molecular weights, functional groups, topology, *etc.* [7-10]. Living polymerization methods, such as ring-opening polymerization (ROP), atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP), and reversible addition-fragmentation chain transfer radical polymerization (RAFT) have been used to design miktoarm star-shaped polymers due to the wide variety of applicable monomers and mild polymerization conditions [11]. Click chemistry provides a powerful method for the synthesis of polymers with unique structures during recent years because this method has unique advantages, such as high specificity, high yields, and near-perfect progress in the presence of most functional groups [12-14]. Therefore, by a combination of living polymerization methods and click chemistry, a wide range of miktoarm star-shaped copolymers, with various chemical compositions and molecular topologies such as AB_2 , A_2B_2 , A_3B_3 , ABC, and so on [15-23], can be synthesized. One of the basic strategies for the synthesis of star polymers is called the arm-first method. In this strategy, reactive linear chains are linked to a central core having certain functional groups [24-31].

Energetic materials are generally organic compounds that contain energetic groups, such as $-NO_2$, $-ONO_2$, $-N_3$ and others, in their molecular structure. These materials produce a lot of energy when undergoing decomposition [32]. Energetic materials (glycidyl azide polymer (GAP), PGN, *etc.*) are rarely used in their pure form, but are used in conjunction with inert materials, *e.g.* HTPB, poly(ϵ -caprolactone) (PCL), *etc.*, in explosive and propellant formulations [33]. The application of inert polymers for explosive and propellant formulations decreases the overall energy of such systems [34].

In the present study, we report the synthesis of A_2B_2 -type energetic miktoarm star-shaped polymers containing PCL with GAP. We synthesized these polymers

by means of ROP and click reaction techniques. The chemical structure of the synthesized miktoarm polymer was confirmed by FT-IR and ^1H NMR spectroscopy and GPC. To the best of our knowledge, the synthesis of A_2B_2 type energetic miktoarm star-shaped copolymers with linear PCL along with GAP as energetic blocks have not been reported.

2 Materials and Methods

ϵ -Caprolactone (ϵ -CL) (Aldrich), stannous 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) (Aldrich), 2,2-bis(bromomethyl)-1,3-propanediol (Aldrich), propargyl alcohol (99%, Merck), epichlorohydrin (99%, Merck), sodium azide (Merck). Solvents dichloromethane (CH_2Cl_2), dimethylformamide (DMF), ethanol and tetrahydrofuran (THF) were distilled over drying agents under nitrogen before use.

The IR spectra were recorded on a Nicolet800 spectrometer in the range 400–4000 cm^{-1} . ^1H NMR spectra were recorded on a Bruker DPX-250 instrument operating at 500 MHz and using CDCl_3 as the solvent; chemical shifts were reported in δ (ppm) from TMS. T_g was measured by DSC (DSC200F3t-sensor/E, Perkin-Elmer). All tests were performed under a nitrogen atmosphere (20 mL/min) at a heating rate of 10 K/min over the temperature range -100 to 308 $^\circ\text{C}$. Thermogravimetric analysis (TGA, SDT Q600 V20.9 Build 20) was performed at a heating rate of 10 K/min from 25 – 500 $^\circ\text{C}$ with an argon flow rate of 50 mL/min. Derivative thermal gravimetry (DTG) data were obtained from the TGA. Gel Permeation Chromatography (GPC) was conducted using 10 μm PL gel columns using a GPC Agilent 1100 (USA) with a refractive index detector, using an Agilent PLgel 5 μm mixed-C 300×7.5 mm column, THF was used as the solvent, injected at 30 $^\circ\text{C}$, at 1 mm/min, and calibrated with polystyrene as standard.

3 Synthesis

3.1 Synthesis of dibromo end-functionalized PCL [(PCL) $_2$ -(Br) $_2$]

In a dried and nitrogen-purged Schlenk flask equipped with a magnetic stirrer were placed 2,2-bis (bromomethyl)-1,3-propanediol (3.38 g, 0.0129 mol) and ϵ -CL (25 g, 0.22 mol). The contents of the flask were stirred vigorously until a homogenous mixture was obtained. Stannous 2-ethylhexanoate (0.964 g, 0.00238 mol) dissolved in hexane (1 mL) was then injected into the flask by

means of a syringe. The flask was charged with N_2 and the reaction mixture was allowed to stir for 2 days at $110\text{ }^\circ\text{C}$. The reaction mixture was cooled to room temperature and then dissolved in CH_2Cl_2 to obtain a viscous solution. The solution was added dropwise to a beaker containing cold ethanol (200 mL) and the precipitated polymer was collected by filtration, washed with cold ethanol and dried under vacuum at room temperature to obtain $(\text{PCL})_2\text{-(Br)}_2$. Yield: 27 g, 95%.

3.2 Azidation of dibromo end-functionalized PCL [$(\text{PCL})_2\text{-(N}_3)_2$]

In a 2-necked round-bottomed flask equipped with a magnetic stirrer, dibromo end-functionalized PCL [$(\text{PCL})_2\text{-(Br)}_2$] (1.37 g, ~ 0.37 mmol) was dissolved in DMF (7 mL) by slight heating. NaN_3 (351 mg, 5.4 mmol) was then added and the reaction suspension was stirred for 60 h at $55\text{ }^\circ\text{C}$. The reaction mixture was filtered through a filter paper and washed with CH_2Cl_2 to remove the excess solid NaN_3 . The clear filtrate was concentrated under vacuum and then added dropwise to cold ethanol (50 mL) with stirring. The white polymeric precipitate, diazido end-functionalized PCL, [$(\text{PCL})_2\text{-(N}_3)_2$], was filtered off, washed with cold ethanol and dried under vacuum at room temperature.

3.3 Synthesis of propargyl- terminated PECH (PTPECH)

For the synthesis of PTPECH, propargyl alcohol (1.12 g, 0.02 mol) and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.75 mL, 6.25 mmol) were introduced into a 3-necked flask equipped with a magnetic stirrer and thermometer. This mixture was stirred for 1 h under nitrogen at $0\text{--}5\text{ }^\circ\text{C}$. A solution of epichlorohydrin (22 g, 0.24 mol) in CH_2Cl_2 (70 mL) was added dropwise to this reaction mixture; the duration of this process was over 5 h. The reaction mixture was stirred at $0\text{--}5\text{ }^\circ\text{C}$ for 1 h. Thereafter, the reaction was completed by adding saturated NaCl solution (100 mL). The organic layer was separated and washed with saturated NaHCO_3 solution (4×100 mL), dried over Na_2SO_4 , and filtered and concentrated *in vacuo* to produce PTPECH (20 g, 87% yield).

3.4 Synthesis of A_2B_2 -type miktoarm star copolymers by click chemistry [$(\text{PCL})_2\text{-(PECH)}_2$]

[$(\text{PCL})_2\text{-(N}_3)_2$] (1.53 g, 0.28 mmol) was placed in a round bottom flask with stirrer and PTPECH (0.58 g, 0.58 mmol) was added to the flask. The reaction mixture was dissolved in acetonitrile (10 mL), heated to $90\text{ }^\circ\text{C}$ with stirring in an oil bath, and maintained at this temperature for 72 h.

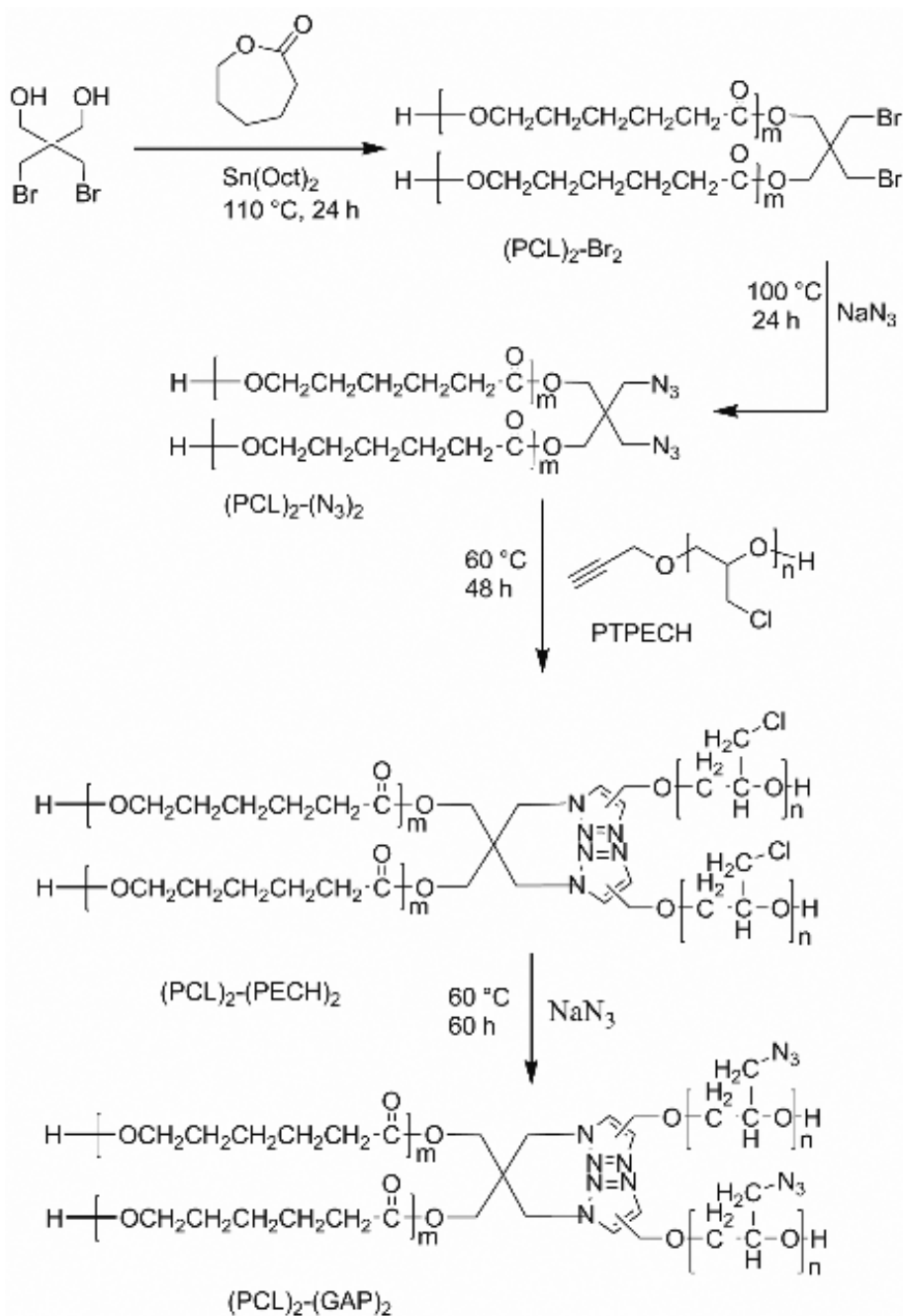
3.5 Azidation of [(PGN)₂-(PECH)₂] and synthesis of [(PCL)₂-(GAP)₂]

The [(PCL)₂-(PECH)₂] obtained from the previous step was dissolved in DMF (30 mL). The reaction mixture was heated to 90 °C, with stirring in an oil bath and NaN₃ (0.45 g, 7 mmol) was added to the mixture. The reaction mixture was heated under reflux for 30 h. Thereafter, the reaction was frozen by adding distilled water. The unreacted azide and salted out sodium chloride were filtered off. The organic phase containing [(PCL)₂-(GAP)₂] was extracted into CH₂Cl₂ and washed several times with distilled water. The washed organic phase was dried over Na₂SO₄, filtered, and the solvent evaporated off under vacuum. [(PCL)₂-(GAP)₂] was obtained (1.7 g, 82% yield).

4 Results and Discussion

4.1 Synthesis of dibromo and diazido end-functionalized PCL

Dibromo end-functionalized PCL [(PCL)₂-(Br)₂] was synthesized by ROP of the ϵ -CL as the monomer. 2,2-Bis(bromomethyl)-1,3-propanediol with two hydroxyl groups was chosen as the initiator in order to produce two-arm dibromo end-functionalized polymers as seen in Scheme 1. The molar ratio of 2,2-bis(bromomethyl)-1,3-propanediol to ϵ -CL was 1/17. The replacement of the bromine atoms by azide groups was carried out by an azidation reaction with NaN₃ in DMF at 110 °C as shown in Scheme 1. The [(PCL)₂-(N₃)₂] was then reacted with PTPECH by a click reaction at 90 °C under catalyst-free conditions. Finally, the chlorine atoms were replaced by azide groups with NaN₃ in DMF at 110 °C.



Scheme 1. Synthesis route of [(PCL)₂-(GAP)₂]

Table 1. Results for the synthesized polymers

Polymer	Conversion [%]	M_n [g/mol]		M_n expr [g/mol]	M_w/M_n
		M_n (theo) ^{a)}	M_n (HNMR) ^{b)}		
[(PCL) ₂ -(Br) ₂]	95	2103	5735	–	–
[(PCL) ₂ -(N ₃) ₂]	96	2027	5660	5436	1.36
PTPECH	87	1022	1121	1004	1.18
[(PCL) ₂ -(GAP) ₂]	>99	6056	7742	6116	1.25

^{a)} M_n (theo) is the theoretical number average molecular weight, ^{b)} M_n (HNMR) is the ¹H NMR molecular weight of each polymer

Structural characterization of the [(PCL)₂-(GAP)₂] was confirmed by FT-IR and ¹H NMR spectroscopic analyses. The FT-IR spectra of PTPECH, [(PCL)₂-(Br)₂], [(PCL)₂-(N₃)₂], [(PCL)₂-(PECH)₂] and [(PCL)₂-(GAP)₂] are shown in Figure 2. The FT-IR spectrum of PTPECH exhibited absorption peaks at 3298, 2117, 1109 cm⁻¹ due to C_{sp}-H, C≡C, and C-O-C stretching vibrations, respectively. The characteristic ester carbonyl group signal of the dibromo- and diazido-PCL appeared at 1724 cm⁻¹ as shown in Figure 2. After the reaction of the bromine-functionalities of the polymers with NaN₃, the appearance of a new signal at around 2107 cm⁻¹ demonstrated the presence of azide groups in the [(PCL)₂-(N₃)₂]. In the next stage, the [(PCL)₂-(N₃)₂] was reacted with PTPECH under free-conditions click chemistry. As seen from the FT-IR spectrum of [(PCL)₂-(PECH)₂], the absorption peak at 3298 and 2117 cm⁻¹ are absent. So the click reaction has been successful. Subsequently, azidation of [(PCL)₂-(PECH)₂] was carried out with NaN₃ in DMF at 90 °C. In the FT-IR spectrum of [(PCL)₂-(GAP)₂], the absorptions at 2101 and 1732 cm⁻¹ are attributed to -N₃ and carbonyl groups, respectively.

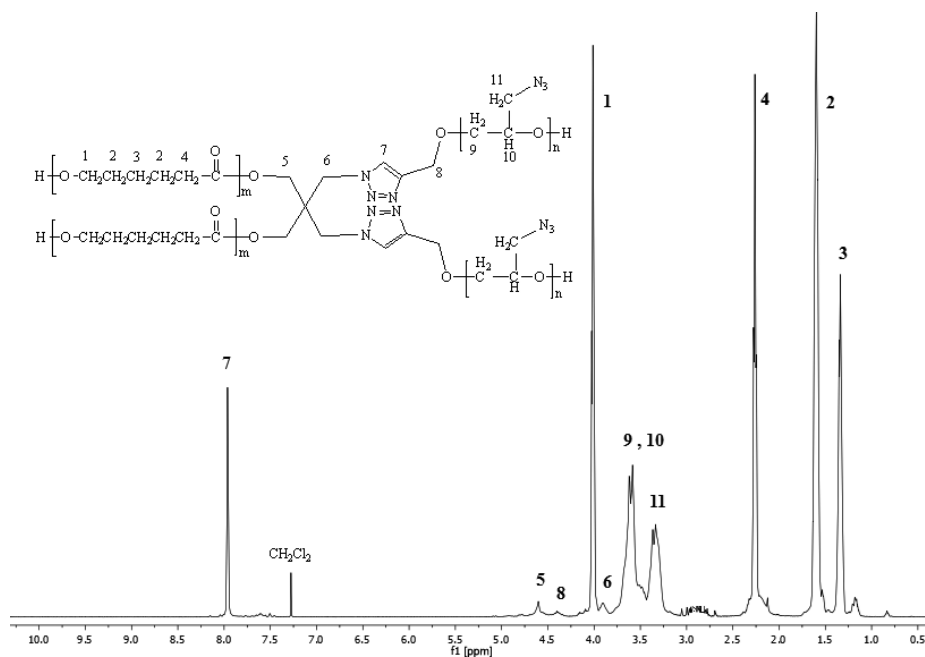


Figure 1. ^1H NMR spectra of $(\text{PCL})_2\text{-(GAP)}_2$

From the ^1H NMR spectrum of $[(\text{PCL})_2\text{-(GAP)}_2]$ shown in Figure 1, the typical signals of the $-\text{O}-\text{CH}_2-$ and $-\text{CH}_2-$ triazole ring protons of the terminal groups from the initiator (2,2-bis(bromomethyl)-1,3-propanediol), were clearly detected at 4.60 ppm (6 protons) and at 3.90 ppm (7 protons), respectively. The peaks for the $-\text{CH}_2\text{O}-$ and $-\text{CH}_2-$ protons of the PCL backbone were also observed at 4.02–3.99 and 2.33–2.23, 1.63–1.53, 1.36–1.33 ppm, respectively. Two peaks appeared at 7.27 and 7.96 ppm, which were assigned to the triazole ring hydrogens. The peaks for the $-\text{CH}_2-\text{N}_3$ and $\text{O}-\text{CH}_2$ protons of GAP were observed at 3.31–3.36 and 3.57–3.62 ppm, respectively. These results indicate the successful synthesis of $[(\text{PCL})_2\text{-(GAP)}_2]$.

The ^1H NMR spectral analyses provided a facile method for calculating the degree of polymerization (DP_n) of each polymer arm and the $M_n(\text{HNMR})$ of the PCL polymers. The DP_n of PCL per polymer arm was found to be 24. The DP_n for a polymer arm was calculated by comparing the integral ratio of the $-\text{CH}_2-$ (from PCL) protons in the repeating polymer units to those of the terminal $-\text{CH}_2-\text{Br}$ protons, based on the ^1H NMR spectra. The $M_n(\text{HNMR})$ of $[(\text{PCL})_2\text{-(GAP)}_2]$ and the DP_n of polymer arm could be calculated using the following formulas:

$$M_n(\text{HNMR}) = DP_n \times M_m \times 2 + M_1 \quad (1)$$

$$DP_n = I_P/I_1 \quad (2)$$

where DP_n is the degree of polymerization of each polymer arm, I_P represents the integral values of the signals of the $-\text{CH}_2-$ protons in the PCL backbone, I_1 represents the integral values of the signals of the $-\text{CH}_2-$ protons in the initiator unit at the end of the PCL chains, M_m is the molecular weight of the ε -CL monomer, M_1 represents the molecular weight of the initiator unit at the terminal groups of the PCL chains.

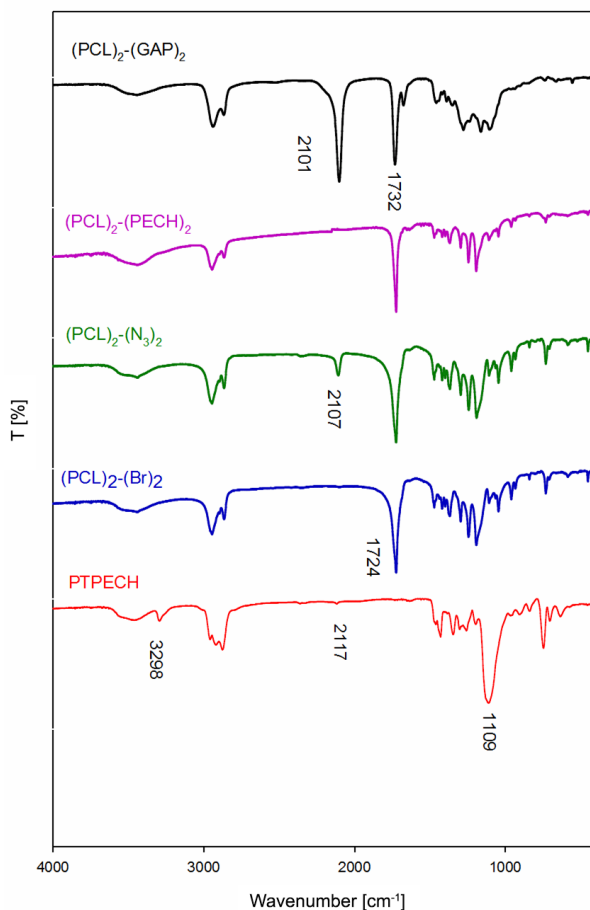


Figure 2. FT-IR spectra of PTPECH, [(PCL)₂-(Br)₂], [(PCL)₂-(N₃)₂], [(PCL)₂-(PECH)₂], [(PCL)₂-(GAP)₂]

The $M_n(\text{theo})$ of the resulting PTPECH and $(\text{PCL})_2\text{-(GAP)}_2$ were calculated using the following equation:

$$M_n(\text{theo}) = [M]_0/[I]_0 \times M_m \times \text{Conversion} + M_I \quad (3)$$

where $[M]_0$ and $[I]_0$ are the initial molar concentrations of monomer ($\epsilon\text{-CL}$) and initiator (2,2-bis(bromomethyl)-1,3-propanediol); M_m and M_I are the molecular weights of the monomer ($\epsilon\text{-CL}$) and the initiator (2,2-bis(bromomethyl)-1,3-propanediol). The theoretical molecular weight of $[(\text{PCL})_2\text{-(N}_3)_2]$ were obtained by subtracting 76 from the theoretical molecular weights of $[(\text{PCL})_2\text{-(Br)}_2]$. All data are summarized in Table 1.

4.2 Thermal decomposition of $(\text{PCL})_2\text{-(GAP)}_2$

Figure 3 shows the DSC thermograms of GAP and $(\text{PCL})_2\text{-(GAP)}_2$. The glass-transition temperature (T_g) of the synthesized copolymer is listed in Table 2. As shown in Table 2, the T_g of GAP and $[(\text{PCL})_2\text{-(GAP)}_2]$ were -47.8 and -51.8 °C, respectively. The copolymerization of PGN with PCL decreases the T_g of PGN. The overall thermal behaviour and decomposition temperature of the synthesized polymer are summarized in Table 2.

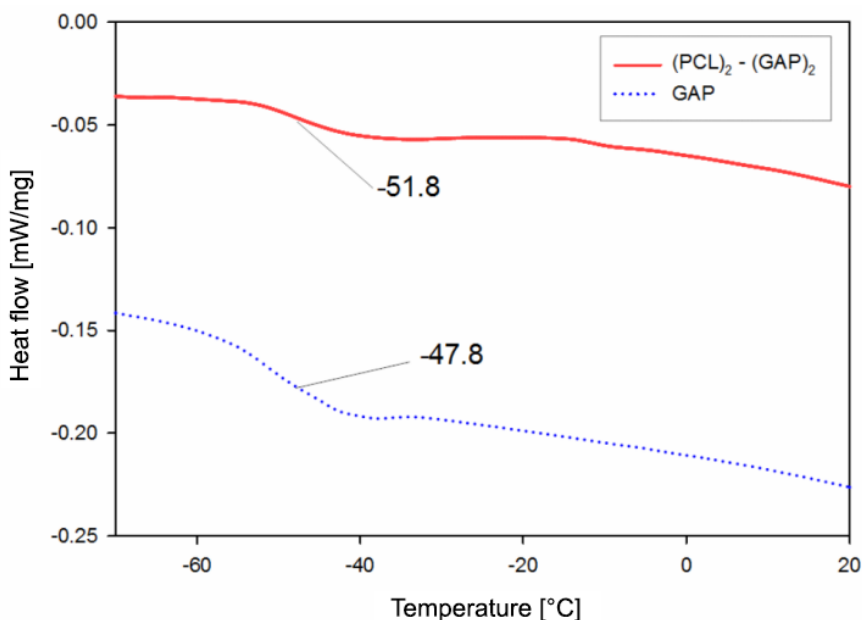


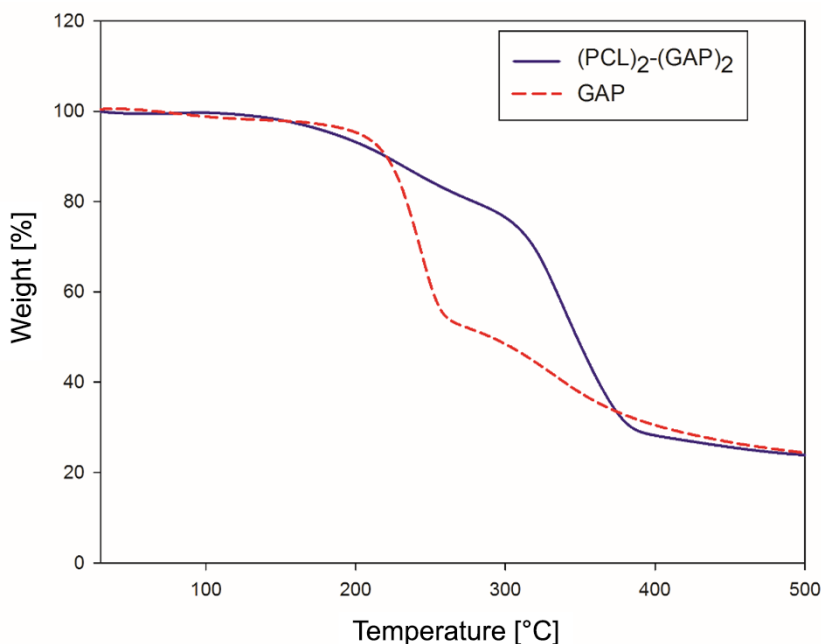
Figure 3. DSC thermograms of GAP and $[(\text{PCL})_2\text{-(GAP)}_2]$ at 10 K/min

Table 2. Thermal properties and decomposition temperatures of the polymers

Polymer	T_g [°C]	T_m [°C]	T_{in}^a [°C]	T_{max}^b [°C]
GAP	-47.8	–	–	–
$[(PCL)_2-(GAP)_2]$	-51.8	59.8	200	357.3

^{a)} The initial decomposition temperature, ^{b)} The temperature corresponding to the maximum rate of weight loss

Figure 4 shows the thermal curves of GAP and $[(PCL)_2-(GAP)_2]$ recorded at 10 °C/min. In the TGA curve of $[(PCL)_2-(GAP)_2]$, two specific weight loss steps were observed. The first step started at 200 °C, ending at 285 °C, and corresponded to the decomposition of $-N_3$. The second step involved the decomposition of the PCL arms between 300 and 400 °C. These two weight loss stages are clearly depicted in the derivative thermogram (Figure 5).

**Figure 4.** TGA curves of GAP and $[(PCL)_2-(GAP)_2]$

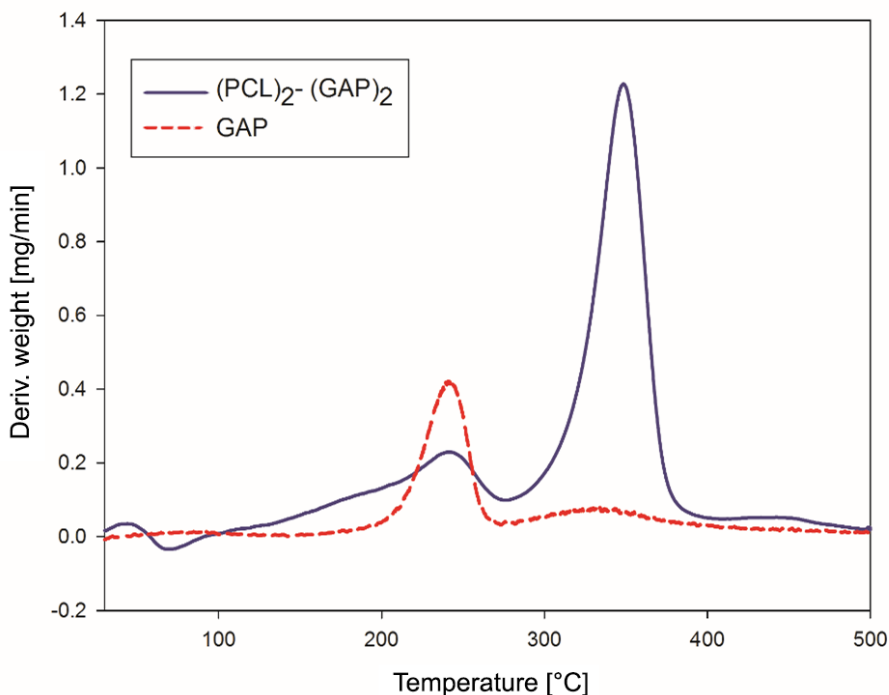


Figure 5. DTGs of GAP and [(PCL)₂-(GAP)₂]

Figure 6 shows the DSC thermogram of [(PCL)₂-(GAP)₂]. The DSC thermogram of [(PCL)₂-(GAP)₂] was measured under an argon atmosphere at a heating rate of 10 °C/min, from room temperature to 500 °C, and exhibited three peaks. An endothermic peak is seen at around 48.95 °C and is attributed to the melting point of the copolymer, the second peak is exothermic at 258.67 °C and is attributed to decomposition of the azide groups. The energy liberated at this stage was 548.9 J/g. The third peak is endothermic at 364.93 °C and is related to degradation of PCL with heat absorption (118.5 J/g).

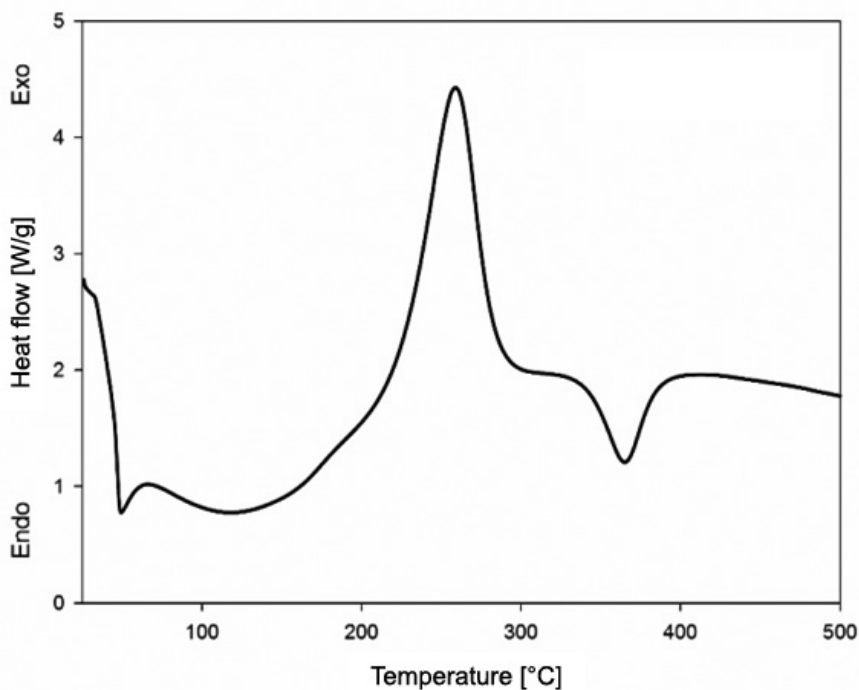


Figure 6. DSC thermogram of (PCL)₂-(GAP)₂

5 Conclusions

- ◆ An A₂B₂-type energetic miktoarm star-shaped polymer containing PCL with GAP has been synthesized by using controlled/living ring opening polymerization and click chemistry. The structure was characterized by spectral and GPC measurements.
- ◆ The thermal behaviour of the synthesized polymer was investigated by differential scanning calorimetry and thermogravimetric analysis (DSC/TGA). This A₂B₂ star-type energetic copolymer decomposes in two stages. The first stage is attributed to decomposition of the azide groups and the second stage is related to decomposition of the PCL arms. The peaks of each stage were at 251 and 355 °C, respectively. The melting point of the copolymer was 48.9 °C.

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