



Synthesis and Kinetic Study of a PCL-GAP-PCL Tri-block Copolymer

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Abstract: An energetic tri-block copolymer PCL-GAP-PCL ($M_n = 1794$) was synthesized by a ring-opening polymerization of ϵ -caprolactone with glycidyl azide polymer (GAP) of low molecular weight ($M_n = 1006$ g/mol) as initiator, in the presence of dibutyltin dilaurate (DBTDL) as catalyst, at 100 °C in the absence of solvent. The products obtained in high yield were characterized by FTIR, gel permeation chromatography (GPC), and ^1H and ^{13}C NMR spectroscopy. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were used to study the thermal behaviour of the polymers. An advanced isoconversional method has been applied for kinetic analysis. The activation energy, calculated by the Flynn-Wall-Ozawa (FWO) and Kissinger methods, and thermal analysis revealed that the tri-block copolymer has greater thermal stability than homopolymer GAP. The results of the activation energies from the Kissinger method for the first and second steps were 180.3 kJ·mol $^{-1}$ and 209.8 kJ·mol $^{-1}$, respectively. Furthermore, for the copolymer, the activation energy *versus* the level of conversion was calculated by the FWO method. The glass transition temperature (T_g) for GAP was influenced by the PCL blocks; as a result the copolymer ($T_g = -64$ °C) showed better thermal properties than homopolymer GAP ($T_g = -48$ °C).

Keywords: poly(glycidyl azide), poly(caprolactone), copolymer, kinetic study, activation energy

1 Introduction

Glycidyl azide polymer (GAP) is a promising candidate as an energetic binder and energetic plasticizer, to increase the burn rate (BR), specific impulse *etc.* in ammonium nitrate, nitramide, nitramine and perchlorate propellant systems,

because of its positive heat of formation and high density. It has potential to produce chlorine-free, low polluting propellants in conjunction with ammonium nitrate as the oxidizer [1, 2].

Although GAP is a well-known and promising energetic polymer, propellants based on it suffer from poor mechanical and low-temperature properties [3]. To overcome these problems, plasticized GAP-based copolymeric binders have been prepared and investigated through the incorporation of flexible structural polyethylene glycol (PEG) [4] and poly(caprolactone) (PCL) [5, 6] units, and the incorporation of oligomer-type GAP, especially chain-end, azide-terminated GAP, as an energetic plasticizer [7, 8].

In order to improve the mechanical and thermal properties of GAP, it is beneficial to prepare a copolymer of it with a polymer with good mechanical and thermal properties, such as polycaprolactone (PCL). PCL is a semicrystalline, biodegradable polymer belonging to the aliphatic polyester family. It is more interesting than other aliphatic polyesters because of its good thermoplastic processing properties. A low glass-transition temperature and a high decomposition temperature, with a wide range of temperatures that allow extrusion, are among its most important advantages [9-11].

Although the thermal behaviour and kinetics parameters of GAP polymers have been studied [6, 8, 12, 13], the kinetic aspects of the thermal degradation of new polymers based on it are not known. The importance of reliable thermal analysis cannot be disregarded, so finding a reliable approach to the kinetic analysis of these materials allows material applications over a considered temperature range to be realized.

In this study, we wanted to synthesise and investigate the thermal behaviour and degradation kinetics of the tri-block copolymer PCL-GAP-PCL. The degradation kinetics will be quantified by the Flynn-Wall-Ozawa (FWO) and Kissinger isoconversional methods under non-isothermal conditions. The possible reliable kinetic parameters including activation energies (E_a) will be determined for each conversion (α) by the FWO method and the two stages of degradation by the Kissinger method.

2 Experimental

2.1 Materials

ϵ -Caprolactone (Aldrich) was dried over CaH_2 and distilled under reduced pressure prior to use. Polycaprolactone (PCL) with $M_w = 2000$ g/mol was purchased from Aldrich. Dibutyltin dilaurate (DBTDL) of 96% purity, epichlorohydrin (ECH),

BF₃-diethyl ether complex, sodium sulfate, and n-hexane were purchased from Merck. 1,4-Butanediol (BDO) was purchased from Fluka. Dimethyl formamide (DMF), purchased from Sigma-Aldrich, and methylene chloride, from Mojallali, was dried with CaH₂ (Merck) and distilled under reduced pressure.

2.2 Instruments and measurements

The IR spectra were recorded with a Nicolet 800 spectrometer in the range 400–4000 cm⁻¹. ¹H and ¹³C NMR spectra were recorded with a Bruker DPX-250 instrument operating at 250.13 MHz and using CDCl₃ as solvent; chemical shifts were reported in δ (ppm) from TMS. Thermogravimetric (TG), isothermal TG and differential scanning calorimetric (DSC) analyses were performed using a PerkinElmer STA 6000 instrument and alumina pans under an argon atmosphere with temperature programmed rates of 10 °C·min⁻¹, 20 °C·min⁻¹, 30 °C·min⁻¹ and 40 °C·min⁻¹, from room temperature to 700 °C. The sample masses were ~12 mg for the copolymer and ~3 mg for GAP. The glass transition temperature (T_g) measurements were performed using a DSC 200F3 instrument under an N₂ flow of 20.0 mL/min and a heating rate of 10 °C min⁻¹, from -100 °C to 10 °C. The T_g was computed as the midpoint of the heat capacity increase. Gel Permeation Chromatography (GPC) was performed using 10 μ m PL gel columns using a GPC Agilent 1100 (USA) instrument with a refractive index detector, using an Agilent PLgel 5 μ m mixed-C 300 mm \times 7.5 mm column; THF was used as the solvent and injected at 30 °C at the rate of 1 mL/min, and calibrated with polystyrene standard.

2.3 Synthesis of GAP with low molecular weight

GAP was synthesized in two steps. The first step was the synthesis of polyepichlorohydrin (PECH) of low molecular weight. The second step was the conversion of PECH polymer to GAP [14]. Butanediol (BDO) (2.7 g, 0.0299 mol) in methylene chloride (50 mL) was added to a 100 mL three-necked flask fitted with a thermometer and nitrogen inlet. BF₃-diethyl ether complex (0.7 mL) was injected into the reaction mixture and stirred at room temperature for 30 min. After cooling the reaction vessel to 0 °C using an ice-salt mixture, epichlorohydrin (25 g, 0.2161 mol) was added dropwise to the reaction mixture over a period of 4 h. The mole ratio of BDO to ECH was 1:9. After the addition of the ECH, the reaction was continued for a further 12 h at room temperature. Thereafter, the organic phase containing PECH was added to distilled water and washed several times until neutral pH was obtained. The washed organic phase was dried over sodium sulfate, filtered and the solvent evaporated under vacuum to obtain PECH (24.85 g, 89.7% yield).

In the second step, PECH (20 g) in DMF (100 mL) was added to a 250 mL three-necked flask fitted with a thermometer, nitrogen inlet, and water condenser. The reaction mixture was heated, with stirring, to 60 °C in an oil bath. Sodium azide (20 g, 0.2768 mol) was added to the mixture over a period of 20 min, then the reaction mixture was heated to 110 °C and the reaction was continued for a further 24 h. Thereafter, the unreacted azide and salted out sodium chloride were filtered off and the solvent was evaporated under vacuum. The resin obtained was dissolved in methylene chloride (50 mL) and washed several times with distilled water until neutral pH. The washed organic phase was dried over sodium sulfate, filtered, and the solvent was evaporated under vacuum. GAP (17.12 g, 85.6% yield) was obtained. GPC analysis: $M_w = 1036$ g/mol, $M_n = 1006$ g/mol, PDI = 1.2; $^1\text{H NMR}$: δ 3.4, 3.66, 2.31, 1.65, 1.41, 4.06 ppm; $^{13}\text{C NMR}$: 78.6, 70.14, 51.5 ppm; FTIR: 3450, 2101, 2925, 2868, 1281, 1121 cm^{-1} .

2.4 Synthesis of tri-block copolymer PCL-GAP-PCL

GAP (5 g) with low molecular weight ($M_n = 1006$ g/mol) was added to a 250 mL three-necked flask fitted with a thermometer and nitrogen inlet. DBTDL (0.01 g) was injected into the reaction mixture and stirred at 60 °C for 60 min in an oil bath. Thereafter, the reaction mixture was heated to 100 °C and ϵ -caprolactone (7.5 g, 0.0650 mol) was added dropwise to the reaction mixture over a period of 30 min. After the addition of ϵ -caprolactone, the reaction was continued for a further 19 h at 100 °C. The reaction mixture was then cooled to room temperature. The resulting resin was dissolved in methylene chloride (50 mL) and washed with n-hexane (4×50 mL). The copolymer solution was dried over sodium sulfate, filtered, and the solvent was evaporated under vacuum to give PCL-GAP-PCL (11.39 g, 91.12% yield). GPC analysis: $M_w = 2865$ g/mol, $M_n = 1794$ g/mol, PDI = 1.59; $^1\text{H NMR}$: δ 3.4, 3.66, 2.31, 1.65, 1.41, 4.06 ppm; $^{13}\text{C NMR}$: 173, 78.6, 64, 34, 28.8, 25.4, 24.5 ppm; FTIR: 3450, 2101, 2943, 2866, 1724, 1100 cm^{-1} .

2.5 Methods for the determination of the activation energy

There are multiple well-known ways to perform kinetic studies of the degradation of polymeric materials. TG in combination with model-free methods is widely used [15-18]. In the Kissinger method, for example, the temperature at the maximum in the derivative weight loss curve (T_m) of experiments at different heating rates (β) is used. $\ln(\beta/T_m^2)$ is then plotted as a function of the reciprocal temperature and the slope is proportional to the activation energy E_a of the degradation step, according to Equation 1 [17, 19, 20].

$$\ln\left(\frac{\beta}{T_m^2}\right) = \frac{-E_\alpha}{R} \frac{1}{T_m} \quad (1)$$

A second model-free approach is the analysis of isothermal and linear non-isothermal TG measurements by an isoconversional method, *i.e.* the Flynn-Wall-Ozawa method. For constant heating rates, the activation energy (E_α) is determined from the slope of the logarithm of the heating rate ($\log\beta$) *versus* the reciprocal temperature corresponding to a selected conversion degree α ($1/T_\alpha$), according to Equation 2 [21-23].

$$\log \beta = C - \left(0.4567 \frac{E_\alpha}{RT_\alpha}\right) \quad (2)$$

where T_α is the temperature at conversion degree (α) and C is a constant.

The TG results are shown as the variation of the sample mass (mass expressed in percent) *versus* temperature or time, or as a derivative mass loss curve corresponding to minus the derivative to temperature of the mass (der. mass in %/°C). The evolution of the mass (expressed in percent) is calculated by Equation 3.

$$\text{mass (\%)} = \frac{(m_t - m_e)}{(m_b - m_e)} \quad (3)$$

where m_t is the mass at a certain reaction time t , m_b the mass at the beginning and m_e the mass at the end of a degradation step or steps. For the FWO kinetic analysis, the mass (%) signal is recalculated into conversion (%) by Equation 4.

$$\text{Conversion (\%)} = 100 - \text{mass (\%)} \quad (4)$$

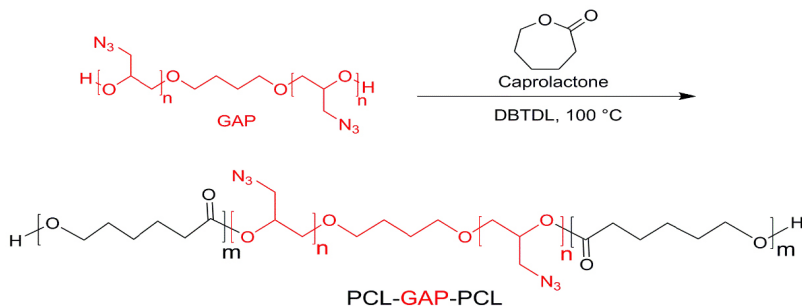
3 Results and Discussion

3.1 Synthesis of the tri-block copolymer PCL-GAP-PCL

GAP ($M_n = 1006$ g/mol) was synthesized *via* PECH diol of low molecular weight. This is due to the fact that a higher molecular weight of the prepolymer would lead to a higher viscosity, and incur high energy costs during the processing operations. We used GAP with a low molecular weight as a macromolecular initiator for the copolymer synthesis. The characterization results for the synthesized GAP polymers are listed in Table 1.

The tri-block copolymer PCL-GAP-PCL ($M_n = 1794$ g/mol) was obtained *via* the ring-opening polymerization of ϵ -caprolactone catalyzed with DBTDL

(without solvent) in the presence of GAP of low molecular weight and with two functional –OH end-groups in each molecular chain (Scheme 1). The characterization results for the synthesized PCL-GAP-PCL polymer are also listed in Table 1.



Scheme 1. Synthesis of PCL-GAP-PCL copolymer

Table 1. Properties of the synthesized GAP and PCL-GAP-PCL

Polymer	T_g	Molecular weight	^{13}C NMR	^1H NMR
GAP	$-48.8\text{ }^\circ\text{C}$	Mw = 1036 g/mol, Mn = 1006 g/mol, PDI = 1.2	$\delta = 78.6$ (CH), 70.1 (CH ₂), 51.5 ppm (CH ₂ N ₃)	$\delta = 3.60$ (3H; –CH ₂ –CH–), 3.40 ppm (2H; –CH ₂ N ₃)
PCL-GAP-PCL	$-64.3\text{ }^\circ\text{C}$	Mw = 2865 g/mol, Mn = 1794 g/mol, PDI = 1.59	$\delta = 173$ (C=O), 78.6 (CH–O), 64 (CH–OCO–), 34 (CH ₂ CO), 28.8, 25.4, 24.5 ppm (–CH ₂ CH ₂ CH ₂ –)	$\delta = 3.40$ (2H; –CH ₂ N ₃), 3.66 (3H; CH ₂ –CH–O–CO–), 2.31 (2H; CO–CH ₂ –), 1.65, 1.41 (6H; –CH ₂ CH ₂ CH ₂ –), 4.06 ppm (2H; CH ₂ –O)

In the synthesis of the copolymer of PCL-GAP-PCL we used GAP as the macro-initiator along with DBTDL as the catalyst. By this route, the GAP will form the central block and the ring opened caprolactone units will be attached to both ends of GAP central block. Conversion of GAP to PCL-GAP-PCL is a ring opening reaction. As shown in Figure 1, the reaction could be easily monitored by FTIR spectroscopy. The appearance of a new stretching band for C=O at 1724 cm^{-1} is evidence that GAP is undergoing ring opening during the polymerization process and the appearance of stronger absorbance at $2866\text{--}2940\text{ cm}^{-1}$ for C–H (of CH₂) implies the successful introduction of the PCL chains. The ^1H NMR spectrum of GAP shows peaks at 3.4 ppm and 3.6 ppm (Figure 2). The ^1H NMR spectrum of the tri-block copolymer PCL-GAP-PCL shows the same characteristic peaks of GAP. Moreover, the characteristic peaks of PCL can also be seen at 1.65 ppm, 1.41 ppm, 2.31 ppm, and 4.06 ppm. These results prove that PCL is attached to GAP.

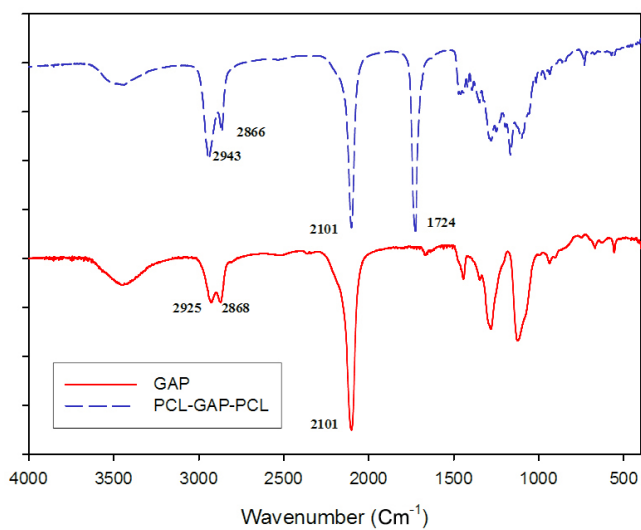


Figure 1. Comparison of the FTIR spectra of GAP and PCL-GAP-PCL copolymer

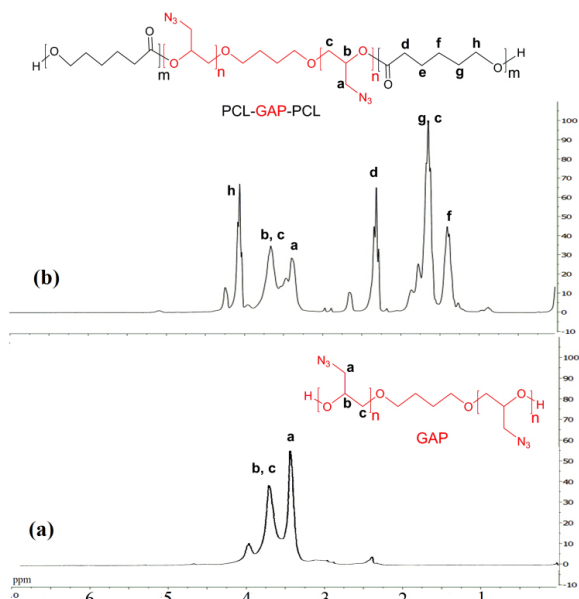


Figure 2. ^1H NMR of (a) GAP and (b) tri-block copolymer PCL-GAP-PCL

3.2 TG, DSC, DTG and activation energy

As an initial investigation of the thermal analysis of GAP and the copolymer, their glass transition temperatures (T_g) were determined. From the DSC runs at a rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, the T_g of GAP of low molecular weight and the copolymer were $-64\text{ }^\circ\text{C}$ and $-48\text{ }^\circ\text{C}$, respectively. Figure 3 shows the glass transition temperature curve of the copolymer ($T_g = -64.3\text{ }^\circ\text{C}$). The results for the tri-block copolymer showed that it had only one T_g and that its T_g was lower than that of GAP.

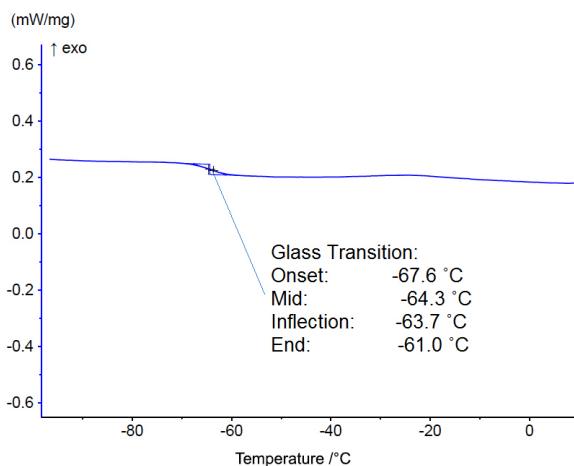


Figure 3. DSC thermogram of the tri-block copolymer PCL-GAP-PCL

Figure 4 shows the DSC curves of GAP and the copolymer samples heated at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, $30\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, and $40\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, from room temperature up to $700\text{ }^\circ\text{C}$. The GAP sample showed two exothermic decompositions with peak temperatures of $245\text{ }^\circ\text{C}$ and $523\text{ }^\circ\text{C}$, which were associated with heat releases of $2153\text{ J}\cdot\text{g}^{-1}$ and $2798\text{ J}\cdot\text{g}^{-1}$, respectively. By contrast, for the copolymer the first exothermic decomposition was at about $255\text{ }^\circ\text{C}$ to $277\text{ }^\circ\text{C}$ (related to heating rate, with heat release from $990.80\text{ J}\cdot\text{g}^{-1}$ to $1089.17\text{ J}\cdot\text{g}^{-1}$), and the second endothermic peak was at about $424\text{ }^\circ\text{C}$ to $451\text{ }^\circ\text{C}$ (related to heating rate, with heat absorption from $418.81\text{ J}\cdot\text{g}^{-1}$ to $1502.70\text{ J}\cdot\text{g}^{-1}$).

The thermal stability and activation energy of the degradation of the polymers were studied by the TG technique. The programmed TG curves under Ar for pure GAP and its copolymer, PCL-GAP-PCL, are shown in Figure 5. GAP and the corresponding tri-block copolymer are stable to approximately $200\text{ }^\circ\text{C}$ and $212\text{ }^\circ\text{C}$, respectively. The results showed that the copolymer has a higher peak degradation temperature compared to the GAP pure polymer. This finding is inconsistent with the findings of Sivalingam *et al.* who studied the pyrolysis

mass analysis of pure PCL [11]. Furthermore, the copolymer decomposed in two stages around 280 °C and 440 °C. The initial mass loss, ~29%, corresponds to the removal of the N₃ groups from the polymeric chain, which is an exothermic decomposition as understood from the DSC thermograms. The second mass loss corresponds to the slow decomposition of the rest of the polymer after the initial N₃ elimination. The latter stage mass loss occurs without any considerable heat release as there is no exothermic peak observed after the decomposition of the energetic groups [12, 13, 24, 25]. Consequently, the tri-block copolymer has more thermal stability than GAP.

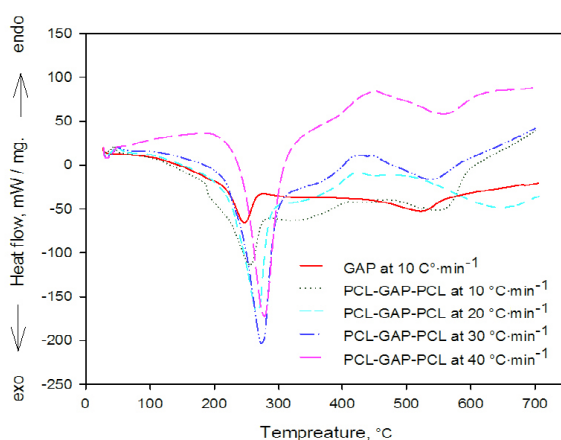


Figure 4. DSC thermograms of GAP and PCL-GAP-PCL samples at various heating rates (10 °C·min⁻¹, 20 °C·min⁻¹, 30 °C·min⁻¹, and 40 °C·min⁻¹)

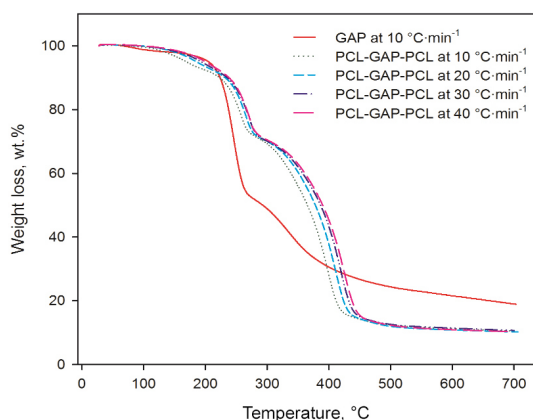


Figure 5. TG thermograms of GAP and PCL-GAP-PCL samples at various heating rates (10 °C·min⁻¹, 20 °C·min⁻¹, 30 °C·min⁻¹, and 40 °C·min⁻¹)

From the DTG results, one peak was observed for GAP and two peaks for the copolymer at different heating rates (Figure 6); whereas at the same heating rates, the two degradation peaks for the tri-block copolymer were at about 255 °C and 451 °C, respectively. One can conclude that attaching the PCL segments to the GAP chains contributes to the magnitude of the peak increases. Persenaire *et al.* [25] showed that the main products of PCL degradation, produced as gases, were H₂O, CO₂, and 5-hexenoic acid. The second step leads to the formation of ϵ -caprolactone (cyclic monomer) as result of an unzipping depolymerization process. The mechanism of thermal degradation of PCL can be interpreted on the basis of two principal phenomena: the first stage is a random chain cleavage of the polymer via *cis*-elimination and the consecutive elimination of monomer from the hydroxyl end of the polymer [23, 26]. Figure 7 shows the TG/DTG/DSC of PCL.

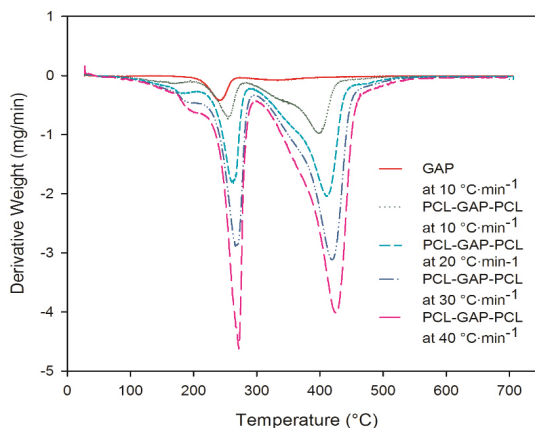


Figure 6. Derivative mass loss (DTG) of GAP and PCL-GAP-PCL samples at various heating rates (10 °C·min⁻¹, 20 °C·min⁻¹, 30 °C·min⁻¹, and 40 °C·min⁻¹)

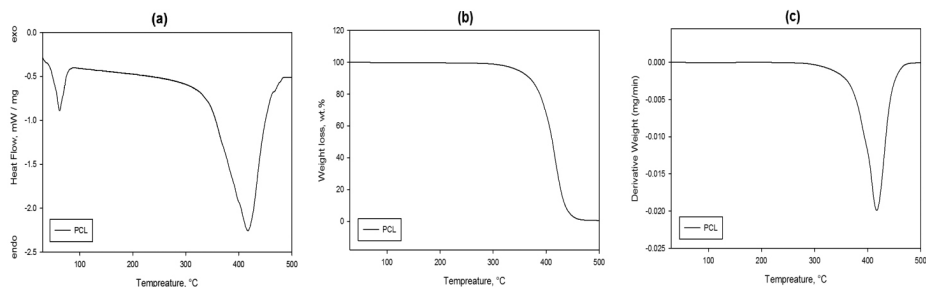


Figure 7. (a) DSC, (b) TGA, (c) DTG of PCL

In Figure 8 the corresponding Kissinger plot is depicted with activation energies for the two step degradation of the copolymer. It was found that the $\ln(\beta/T_m^2)$ against $1/T_m$ plots were straight lines, which indicated that the mechanism of thermal decomposition of these compounds is first order [27]. The slope of the line was equal to $-E_a/R$. Therefore, the activation energy (E_a) was obtained from the slope of the graph [28]. The resulting activation energy for the first step was $180.3 \text{ kJ}\cdot\text{mol}^{-1}$ ($R^2 = 0.95$) and for the second step was $209.8 \text{ kJ}\cdot\text{mol}^{-1}$ ($R^2 = 0.99$). As may be seen from the calculated activation energies, the second step has a higher activation energy than first step ($209.8 \text{ kJ}\cdot\text{mol}^{-1}$ versus $180.3 \text{ kJ}\cdot\text{mol}^{-1}$).

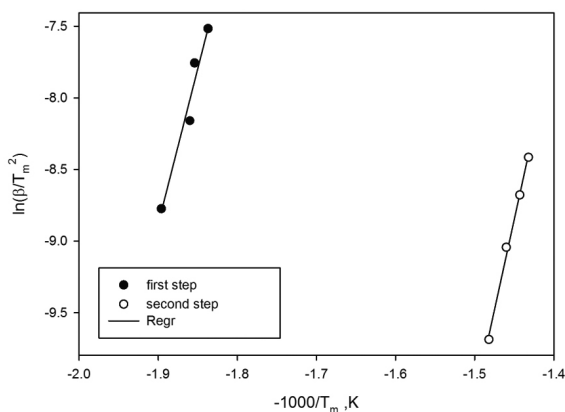


Figure 8. The plot of $\ln(\beta/T^2)$ vs. $1/T_m$

According to the FWO method (Equation 2), the activation energy (E_a) can be obtained at each degree of degradation (α) from the slope of $\log\beta$ (β is heating rate) versus $1/T$ plot (Figure 9). Figure 9 shows the dependence of the activation energy on the degradation degree evaluated for the non-isothermal data (linear heating rate). As may be seen from the diagram, the activation energy for the copolymer increased as the degradation proceeded.

Figure 10 shows the activation energies calculated by the Kissinger and the FWO methods. The Kissinger method uses only the two maximal mass loss rate temperatures for the calculation and we obtained only two values for the entire reaction progress, but the FWO method allowed us to create the activation energy versus level of conversion dependence graph. The activation energy results obtained for different conversion values are displayed in Figure 10. In the cases of the FWO and the Kissinger methods, their progress is obviously similar. In the beginning, the activation energy values calculated by FWO increased along

with the degree of conversion until it reached about 30% conversion. In this zone the values of the activation energy ranged between $72.79 \text{ kJ}\cdot\text{mol}^{-1}$ and $290.72 \text{ kJ}\cdot\text{mol}^{-1}$. In the second zone, the activation energy decreased *versus* conversion until it reached about $180.14 \text{ kJ}\cdot\text{mol}^{-1}$, thereafter the dependence curve increased with a slight slope until it reached $204.95 \text{ kJ}\cdot\text{mol}^{-1}$ at 95% of conversion.

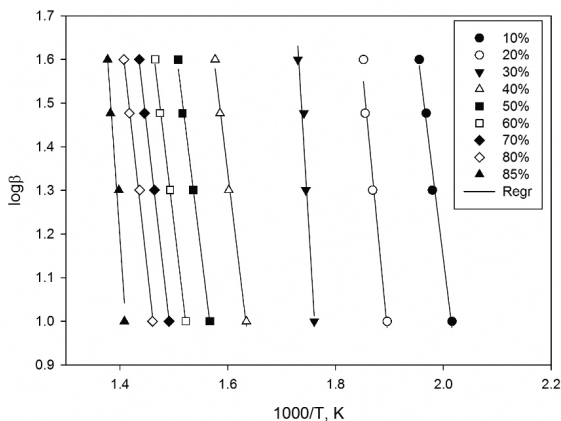


Figure 9. Plots of $\log\beta$ against $1/T$ (FWO method) for selected values of conversion

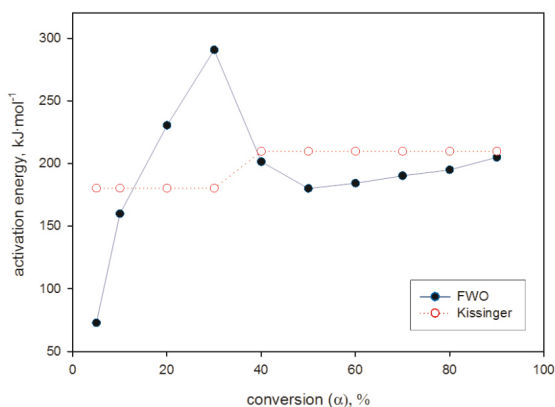


Figure 10. Dependence of activation energy on percentage conversion

4 Conclusions

An energetic tri-block copolymer PCL-GAP-PCL was synthesized using GAP macromolecules as initiator and catalyzed by DBTDL. The GAP sample showed two exothermic decompositions with peak temperatures of 245 °C and 523 °C. By contrast, for the copolymer the first exothermic decomposition was at about 255 °C to 277 °C (related to heating rate) and a second endothermic peak was at about 424 °C to 451 °C, so the thermal stability of the tri-block copolymer PCL-GAP-PCL was greater than that of pure GAP. The activation energy for the copolymer was calculated by the Flynn-Wall-Ozawa (FWO) and Kissinger methods. The activation energy results from the Kissinger method for the first and second steps of degradation were 180.3 kJ·mol⁻¹ and 209.8 kJ·mol⁻¹, respectively. The activation energy *versus* the level of conversion for the copolymer was calculated by the FWO method. The T_g for GAP was influenced by the PCL blocks; as a result the copolymer ($T_g = -64$ °C) showed better thermal properties than GAP ($T_g = -48$ °C).

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