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Ecofriendly synthesis and characterization of carboxylated GAP copolymers†

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Carboxylated GAP copolymers (polyGA-carboxylate) compounds (**1–7**), were synthesized by the simultaneous substitution reaction with PECH, sodium azide, and sodium carboxylate in DMSO. The synthesized compounds (**1–7**) were characterized by various analysis tools, such as Fourier transform infrared (FT-IR), inverse gated decoupling ^{13}C-nuclear magnetic resonance (^{13}C NMR), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), calorimetry, and friction and impact sensitivity. These poly(GA-carboxylate) compounds (**1–7**) have better thermal properties owing to their lower glass transition temperatures, from −48 °C to −55 °C, compared to glycidyl azide polymer (GAP) (−49 °C) and similar first thermal decomposition temperatures (228–230 °C) in comparison to GAP (227 °C), regardless of the introduction of the carboxylate group in GAP. Moreover, poly(GA$_{0.8}$-butyrate$_{0.2}$) and poly(GA$_{0.8}$-decanoate$_{0.2}$) have higher heats of combustion (2331 and 2976 kJ mol^{-1}) and negative formation enthalpies (−0.75 and −2.02 kJ g^{-1}), while GAP has a lower heat of combustion (2029 kJ mol^{-1}) and positive formation enthalpy (1.33 kJ g^{-1}). Therefore, poly(GA-carboxylate) could be a good candidate for the polymeric binder in solid propellants.

1. Introduction

Solid propellants are composed of a polymeric binder, high-energy additives, oxidizers, metallic additives, burn rate modifiers, and so on.[1–3] They are highly energetic and release gaseous products on combustion. Among the ingredients of propellants, polymeric binders play an important role in determining the shape and structural integrity of the propellants.[4,5]

Conventionally, hydroxyl-terminated polybutadiene (HTPB) has been widely used as the propellant binder. The HTPB propellant has a high specific impulse with the ammonium perchlorate (AP) oxidizer. However, the AP-based binders produce HCl gas, causing environmental pollution from the propellant plumes.[6,7]

As new energetic binders to replace the non-energetic HTPB, azide functionalized polymers such as glycidyl azide polymer (GAP), poly[3,3-bis(3-azidomethyl)oxetane] (poly(BAMO)), and poly[(3-azidomethyl)methyloxetane] (poly(AMMO)) have attracted attention as propellant binders.[6,8–11]

GAP contains azide groups as the energetic pendant groups that release heat by exothermic decomposition.[12–14] In addition, it has many advantages over HTPB such as a highly positive heat of formation (+957 kJ kg^{-1}), low sensitivity, high energy, and good compatibility with highly energetic oxidizers such as ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF).[15–18] It provides a higher specific impulse when used in propellant formulations. Furthermore, GAP produces chlorine-free propellant plumes with ammonium nitrate (AN) instead of AP, which can prevent environmental pollution.[19] However, the bulky and polar azide groups in GAP result in a low flexibility of the backbone by the hindrance of motion in the molecular chain.[12] Therefore, GAP has certain drawbacks such as poor low-temperature characteristics.[2,20,21] In addition, GAP is synthesized by the substitution reaction with poly(epichlorohydrin) (PECH) and sodium azide. In this case, an excess sodium azide is typically used to complete the reaction.[22] Because of the use in excess, the residue contains azide groups; it has safety hazards and requires a quenching process with nitrous acid, which produces the toxic nitric oxide (NO) gas. Therefore, it is difficult

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to handle the disposal process during manufacturing; also, a significant cost is involved in handling the liquid waste. To solve these problems and improve the mechanical properties of GAP, GAP copolymers such as fluorinated GAP copolymer, GAP-THF copolymer, and GAP-PEG copolymer has been synthesized.[23–25]

These GAP copolymers have better mechanical properties than GAP owing to the introduction of different monomers or polymers.

Our studies have focused on the improvement of the mechanical properties of GAP and completed substitution reactions so that the extra sodium azide was not left in liquid wastes, thus ensuring ecofriendly reactions. Therefore, some nucleophiles like long-chain carboxylates (butyrate, octanoate, 2-ethyl hexanoate, isononanoate, decanoate) are introduced in the GAP copolymers.

These GAP copolymers are analyzed by ^{13}C NMR, Fourier transform infrared (FT-IR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), viscosity, sensitivity, calorimetry, and thermogravimetric analysis (TGA) in this study.

2. Results and discussion

2.1 Synthesis and characterization of poly(GA-carboxylate) compounds (1–7)

As mentioned earlier, GAP was generally synthesized by using excess sodium azide with PECH. After the completion of the reaction, the quenching step involving the azide residue has safety hazards and is expensive as part of the manufacturing process. Therefore, we synthesized poly(GA-carboxylate) compounds (**1–7**) in order to reduce the azide residue and improve the mechanical properties of GAP. First, we synthesized poly(GA-carboxylate) compounds (**1–7**) by a two-step reaction arranged in the order of azidation and carboxylation or *vice versa*. In addition, we could simply obtain poly(GA-carboxylate) compounds (**1–7**) by addition of a quantitative amount of sodium azide and sodium carboxylate together with PECH in DMSO. When compared with the reaction using excess sodium azide, our synthesis procedure using a quantitative amount of sodium azide very rarely produced gases during the quenching of the azide residue. This could facilitate a safer and inexpensive quenching process.

Reaction monitoring and composition. The reactions were monitored by FT-IR for the reaction times of 1 h, 4 h, 8 h, 12 h and 24 h (Fig. 1). Compared with PECH as a starting material, the azide N=N=N stretching band at 2092 cm^{-1} and ester C=O stretching band at 1733 cm^{-1} increased, while the C–Cl stretching band at 749 cm^{-1} disappeared as the reactions proceeded to completion. Specifically, there was no significant change in the intensity of the azide stretching band for reaction time of 4 h, while intensity of the ester C=O stretching band increased up to the reaction time of 24 h. In other words, azidation was faster than esterification in PECH. Consequently, we fixed the reaction time as 24 h.

The composition of the polymer was analyzed by a quantitative ^{13}C NMR study based on inverse gated decoupling ^{13}C NMR.[26,27] The structures and successful synthesis of poly(GA-carboxylate) compounds (**1–7**) were confirmed from the ^{13}C NMR spectra, and the compositions of poly(GA-carboxylate) compounds (**1–7**) were also measured by inverse gated decoupling ^{13}C NMR spectroscopy. For example, the composition of poly(GA$_{0.7}$-butyrate$_{0.3}$) compound (**1**) was calculated by averaging the integral values of each peak in the inverse gated decoupling ^{13}C NMR spectrum (Fig. 2).

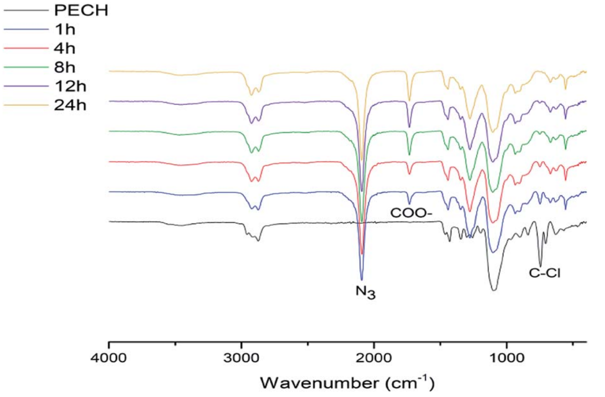


Fig. 1 Monitoring the synthesis of poly(GA$_{0.8}$-butyrate$_{0.2}$) compound (**2**) using FT-IR according to the reaction time (1 h, 4 h, 8 h, 12 h, 24 h).

Average molecular weight. The successful synthesis of poly(GA-carboxylate) compounds (**1–7**) was confirmed by gel permeation chromatography (GPC) to obtain the polydispersity index (PDI) and average molecular weight. First, three different ratios of poly(GA-butyrate) compounds (**1–3**) were synthesized and analyzed by DSC and GPC. Among them, poly(GA$_{0.8}$-butyrate$_{0.2}$) compound (**2**) has the lowest glass transition temperature (−51 °C), and its PDI (1.151) is the closest to 1.000 (Table 1, Fig. 3). Therefore, we chose the poly(GA$_{0.8}$-carboxylate$_{0.2}$) ratio in the case of long-chain carboxylates. Consequently, the substitution reaction yielded good results (84–95% yield), with average molecular weights ranging from 2257 g mol^{-1} to 2611 g mol^{-1}, which represented an increase

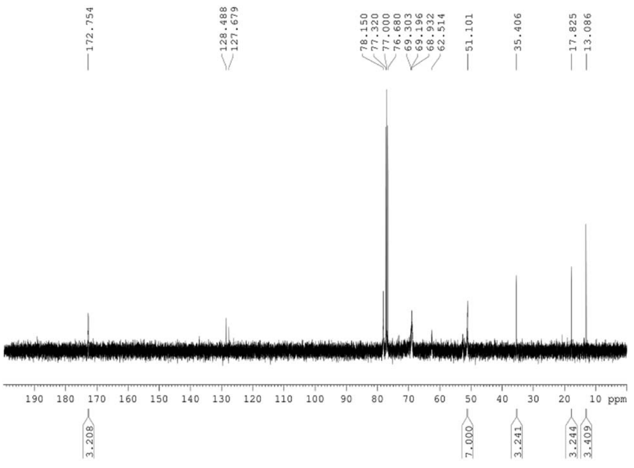
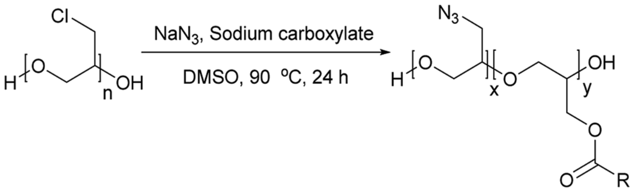


Fig. 2 Inverse gated decoupling ^{13}C NMR spectrum of poly(GA$_{0.7}$-butyrate$_{0.3}$) compound (**1**).

Table 1 Results of substitution reaction using PECH, sodium azide, and sodium carboxylate



Entry	Composition[a]	[Sodium azide] : [sodium carboxylate] mol% (th)	*R*	Yield (%)	M_w[b] (g mol^{-1})	M_n[b] (g mol^{-1})	PDI[b]	T_g[c] (°C)	T_{dec}[d] (°C)
1	PECH	—	—	—	1935	1647	1.175	−39	340
2	Poly(GA$_{0.68}$-butyrate$_{0.32}$) (**1**)	70 : 30	$(CH_2)_2CH_3$	95	2803	2401	1.167	−51	230
3	Poly(GA$_{0.83}$-butyrate$_{0.17}$) (**2**)	80 : 20	$(CH_2)_2CH_3$	89	2334	2396	1.151	−51	228
4	Poly(GA$_{0.93}$-butyrate$_{0.07}$) (**3**)	90 : 10	$(CH_2)_2CH_3$	91	2611	2257	1.157	−49	230
5	Poly(GA$_{0.81}$-2-ethyl hexanoate$_{0.19}$) (**4**)	80 : 20	$CH(CH_2CH_3)(CH_2)_3CH_3$	88	2816	2435	1.154	−54	230
6	Poly(GA$_{0.79}$-octanoate$_{0.21}$) (**5**)	80 : 20	$(CH_2)_6CH_3$	86	2841	2445	1.162	−55	228
7	Poly(GA$_{0.80}$-isononanoate$_{0.20}$) (**6**)	80 : 20	$(CH_2)_5CH(CH_3)_2$	86	2859	2472	1.156	−48	228
8	Poly(GA$_{0.81}$-decanoate$_{0.19}$) (**7**)	80 : 20	$(CH_2)_8CH_3$	84	3029	2611	1.160	−55	230
9	GAP	—	—	—	2143	1853	1.157	−49	227

[a] Calculated by inverse gated decoupling ^{13}C NMR spectroscopy. [b] Measured by GPC. [c] Measured by DSC. [d] Measured by TGA.

from the average molecular weight of PECH (1647 g mol^{-1}) and PDI values that ranged from 1.151 to 1.167 (Fig. 4).

2.2 Thermal properties

Glass transition temperature. As stated above, three different ratios of poly(GA-butyrate) compounds (**1–3**) were first synthesized that have glass transition temperatures (T_g) ranging from −49 °C to −51 °C (Table 1, Fig. 5). In other poly(GA-carboxylate) compounds (**4–7**), the glass transition temperatures were lower than those of poly(GA-butyrate) compounds (**1–3**) (Table 1, Fig. 6) because of the longer alkyl chain. Consequently, most poly(GA-carboxylate) compounds (**1–7**) have similar or lower glass transition temperatures than GAP (−49 °C). Among them, poly(GA$_{0.8}$-octanoate$_{0.2}$) compound (**5**) and poly(GA$_{0.8}$-decanoate$_{0.2}$) compound (**7**) revealed the lowest T_g (−55 °C). This property makes it easier to handle the reaction during processing.

Thermal decomposition. The thermal decomposition temperatures (T_d) of poly(GA-carboxylate) compounds (**1–7**) were measured by TGA for the estimation of their thermal stability. There are two exothermic decomposition steps in poly(GA-carboxylate) compounds (**1–7**) (ESI†). As shown in

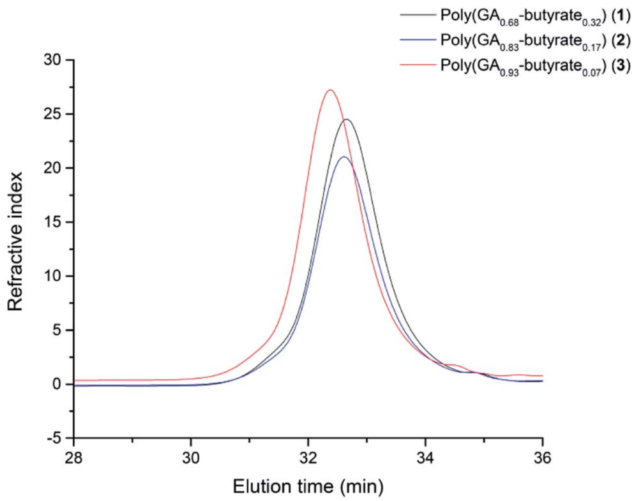


Fig. 3 GPC curves of the three different ratios of poly(GA-butyrate) compounds (**1–3**).

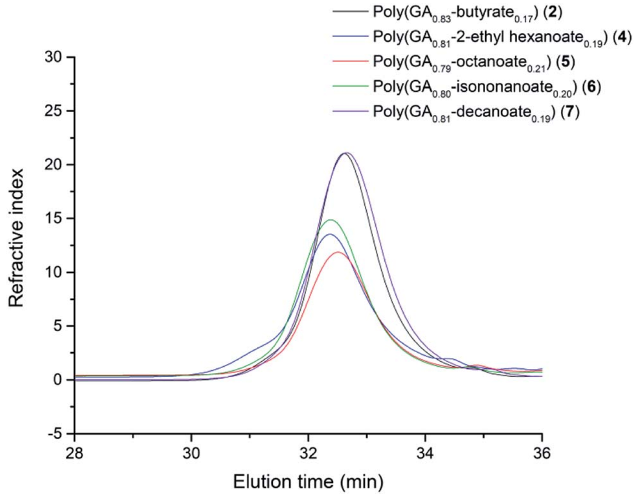


Fig. 4 GPC curves of poly(GA$_{0.8}$-carboxylate$_{0.2}$) compounds (**2, 4–7**) with different carboxylates.

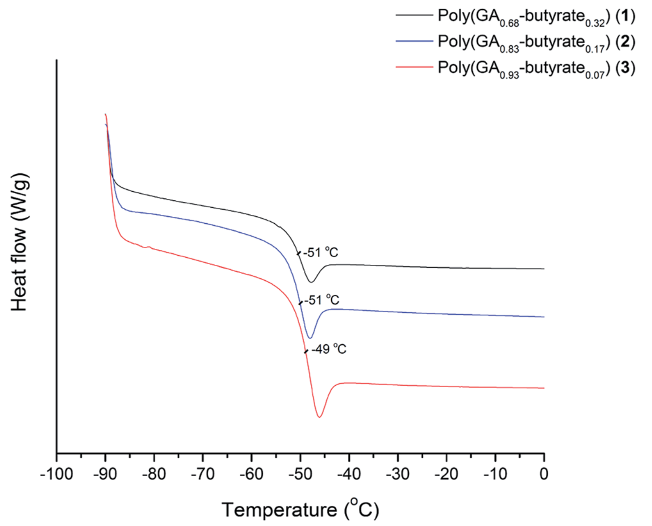


Fig. 5 DSC curves of the three different ratios of poly(GA-butyrate) compounds (**1–3**).

Fig. 7, the first exothermic decomposition of poly($GA_{0.8}$-$decanoate_{0.2}$) compound (**7**) starts at 230 °C, which indicates that poly($GA_{0.8}$-$decanoate_{0.2}$) compound (**7**) was thermally stable up to this temperature. This exothermic decomposition peak was caused by the decomposition of the azide group in the GAP copolymer with the release of nitrogen gas.[25] The second exothermic decomposition occurs at 309 °C, which is attributed to the polyether main chain of poly($GA_{0.8}$-$decanoate_{0.2}$) compound (**7**) and the decanoate group.[28] Additionally, the first exothermic decomposition step of GAP occurs at 227 °C, and the second begins at 329 °C (Table 1). As shown in Table 1, the first decomposition temperatures of the GAP copolymers were similar to that of GAP, which indicates that the carboxylate group survived up to the first decomposition temperature. Therefore, the introduction of the carboxylate group besides the azide group in PECH does not affect the starting temperature of thermal decomposition and the thermal stability.

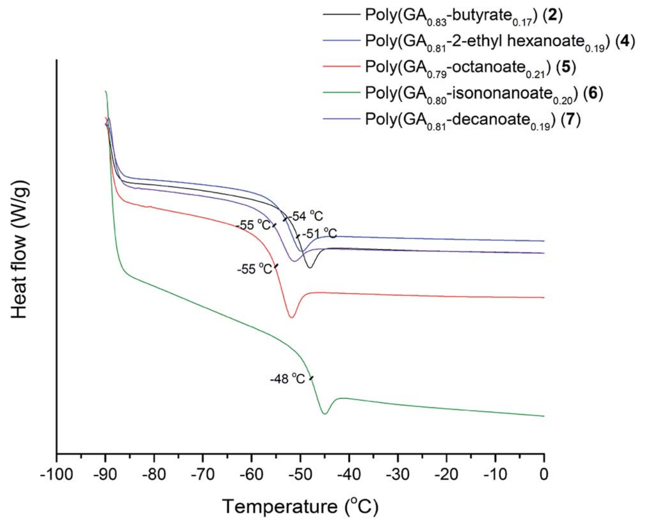


Fig. 6 DSC curves of poly(GA-carboxylate) compounds (**2**, **4–7**) with different carboxylates.

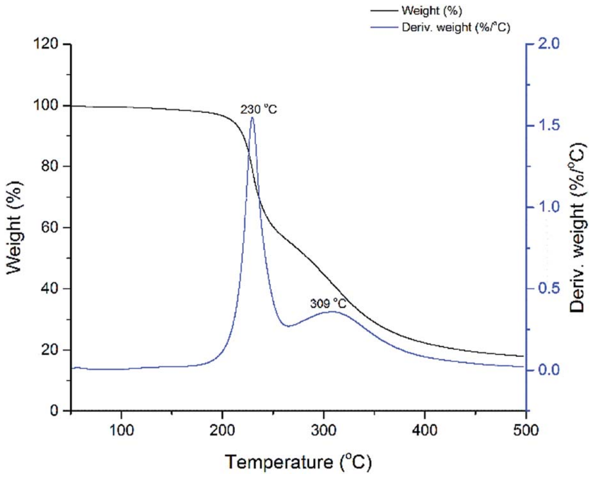


Fig. 7 TGA and DTG curves of poly($GA_{0.8}$-$decanoate_{0.2}$) compound (**7**).

2.3 Viscosity

Viscosity was measured at three different temperatures (25 °C, 40 °C, 60 °C). In general, viscosity has a tendency similar to that of the glass transition temperature (T_g). Poly(GA-carboxylate) compounds (**1–7**) have viscosities ranging from 1400 mPa s to 2230 mPa s at 25 °C, from 497 mPa s to 706 mPa s at 40 °C, and from 160 mPa s to 258 mPa s at 60 °C. The viscosities of most poly(GA-carboxylate) compounds (**1–7**) were lower than that of GAP at any particular temperature (Table 2). In other words, the introduction of the longer non-polar alkyl chain of the carboxylate group in GAP weakens the polarization effect of the azide group in GAP, facilitating the reduction of viscosity. As a result, poly(GA-carboxylate) compounds (**1–7**) have better processabilities in comparison to GAP.

2.4 Energy properties

Heat of combustion and formation. The energies of combustion (ΔU_{comb}) of GAP, poly($GA_{0.8}$-$butyrate_{0.2}$) compound (**2**), and poly($GA_{0.8}$-$decanoate_{0.2}$) compound (**7**) were measured by a Parr Bomb Calorimeter 6200. Then, the combustion enthalpies (ΔH_{comb}) were calculated at 25 °C by using the combustion energies ($\Delta H_{\text{comb}} = \Delta U_{\text{comb}} + \Delta nRT$; $\Delta n = \Delta n_{\text{i}}(\text{product, g}) - \Delta n_{\text{i}}(\text{reactant, g})$). The enthalpies of formation ($\Delta_f H^o$) can be obtained by using the following equation: $\Delta_f H^o(\text{copolymer}) = a\Delta_f H^o(CO_2) + 0.5b\Delta_f H^o(H_2O) - \Delta_c H^o(\text{copolymer})$ (for the composition $C_aH_bN_cO_d$). It is based on the Hess thermochemical cycle at 25 °C with the combustion reactions of the repeating unit. Here, the heat of formation of $H_2O(l)$ is −286 kJ mol^{-1}, and for $CO_2(g)$, is −394 kJ mol^{-1}.[28]

As shown in Table 3, the combustion enthalpies are always negative because combustion is an exothermic reaction. The combustion enthalpies of poly($GA_{0.8}$-$butyrate_{0.2}$) compound (**2**) and poly($GA_{0.8}$-$decanoate_{0.2}$) compound (**7**) have more negative values in comparison to GAP, because they have larger repeating units (greater molar mass) and $|\Delta U_{\text{comb}}|$ in comparison to the

Table 2 Viscosity of poly(GA-carboxylate) compounds (**1–7**) at three different temperatures

Composition	Viscosity[a] (mPa s) @25 °C	Viscosity[a] (mPa s) @40 °C	Viscosity[a] (mPa s) @60 °C
Poly($GA_{0.68}$-butyrate$_{0.32}$) (**1**)	1788	615	216
Poly($GA_{0.83}$-butyrate$_{0.17}$) (**2**)	1956	673	208
Poly($GA_{0.93}$-butyrate$_{0.07}$) (**3**)	2052	690	258
Poly($GA_{0.81}$-2-ethyl hexanoate$_{0.19}$) (**4**)	1972	682	234
Poly($GA_{0.79}$-octanoate$_{0.21}$) (**5**)	1405	520	228
Poly($GA_{0.80}$-isononanoate$_{0.20}$) (**6**)	2230	706	176
Poly($GA_{0.81}$-decanoate$_{0.19}$) (**7**)	1400	497	160
GAP	2500	812	238

[a] measured at the shear rate of 3.84 s^{-1} and 1 rpm.

latter. It suggests that poly($GA_{0.8}$-butyrate$_{0.2}$) compound (**2**) and poly($GA_{0.8}$-decanoate$_{0.2}$) compound (**7**) release higher energies during the combustion process than GAP. Additionally, the enthalpies of formation of poly($GA_{0.8}$-butyrate$_{0.2}$) compound (**2**) and poly($GA_{0.8}$-decanoate$_{0.2}$) compound (**7**) are negative, while that of GAP is positive (1.33 kJ g^{-1}), because poly($GA_{0.8}$-butyrate$_{0.2}$) compound (**2**) and poly($GA_{0.8}$-decanoate$_{0.2}$) compound (**7**) have higher composition of carbons and hydrogens in the repeating unit. In this case, contributions of CO_2 and H_2O terms in the equation of the enthalpies of formation increase beyond the $\Delta_c H^o$ term.[29] Therefore, poly($GA_{0.8}$-butyrate$_{0.2}$) compound (**2**) and poly($GA_{0.8}$-decanoate$_{0.2}$) compound (**7**) have negative formation enthalpies which indicate the product is more stable than the constituent elements. In contrast, the positive formation enthalpy of GAP suggests the opposite.

Sensitivity. Sensitivity, besides thermal stability, is an important property of polymeric binders that determines their application. The friction and impact sensitivity were measured by NATO STANAG 4487 and NATO STANAG 4489, respectively. As shown in Table 4, poly(GA-carboxylate) compounds (**1–3**, **7**) have lower sensitivities with regard to impact than GAP, because the amount of the azide component of poly(GA-carboxylate) compounds (**1–3**, **7**) was lower than that of GAP. Therefore, using poly(GA-carboxylate) compounds (**1–3**, **7**) as a polymeric binder in solid propellants suggest an advantage in terms of safety for the formulation of propellant mixtures.[28]

3. Experimental

3.1 Materials and instruments

Poly(epichlorohydrin) (PECH) was supplied by J. CHEM. Inc. Decanoic acid and octanoic acid were supplied by PMC KOREA CO., LTD. The other chemicals were purchased from commercial sources (Sigma Aldrich, TCI), and were used without further purification, unless specifically mentioned.

For the quantitative analysis of the product, the inverse gated decoupling ^{13}C spectra were measured in $CDCl_3$ with a Bruker NMR and zpig30 pulse program. The Fourier transform infrared (FT-IR) spectra were collected with an Alpha FTIR spectrometer from Bruker using a diamond ATR accessory in the range 4000–400 cm^{-1}. The friction sensitivity was determined using NATO STANAG 4487, and the impact sensitivity was measured by NATO STANAG 4489. Viscosity was obtained from Theo calc T1.2.19 of Brookfield Engineering Labs. Inc. We measured the viscosity at three different temperatures (25, 40, 60 °C), 3.84 (s^{-1}) shear rate, and 1 RPM. DSC was performed on a TA instruments Q 1000 using aluminum pans at the heating rate of 10 °C min^{-1} under nitrogen flow, in the temperature range −90 °C to 20 °C. TGA was performed on a PERKIN ELMER TGA Q500 V6.2 Build 187 under nitrogen atmosphere using a heat rate of 5 °C min^{-1}, in the range 25 °C to 500 °C. The molecular weights of the materials were determined by WATERS 515, with the flow rate of 1.0 mL min^{-1}, using THF as the flow solvent. The heat of combustion was determined by the Parr Bomb Calorimeter 6200.

3.2 General procedure for the synthesis of sodium carboxylate

For the synthesis of sodium carboxylate, THF (50 mL), carboxylic acid (1 mmol), and sodium hydroxide (1 mmol) were added to a 100 mL round-bottom flask. The reaction mixture was stirred at room temperature for 2 h. After the reaction, sodium carboxylate was filtered off, washed with tetrahydrofuran, and dried under vacuum at 40 °C for 24 h.

3.3 General procedure for the synthesis of GAP copolymers based on carboxylate (1–7)

GAP copolymers were synthesized *via* the reaction of PECH, sodium azide, and sodium carboxylate. PECH (50 mmol) was dissolved in DMSO (25 mL) in a 100 mL round-bottom flask at 60 °C. Sodium azide (40 mmol) and sodium carboxylate (10 mmol) were added to the reaction mixture and stirred at 90 °C for 24 h. After the completion of the reaction, the mixture was cooled and 100 mL of ethyl acetate was added. The organic layer was washed with distilled water (100 mL × 4) for the removal of DMSO. The layer was dried over $MgSO_4$ and filtered through a pad of celite, and concentrated under reduced pressure.

Poly($GA_{0.7}$-butyrate$_{0.3}$) (1). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 172.75, 78.15, 69.30, 69.20, 68.93, 62.51, 51.10, 35.41, 17.83, 13.09; IR: 2875, 2094, 1733, 1443, 1278, 1092, 557 cm^{-1}.

Poly($GA_{0.8}$-butyrate$_{0.2}$) (2). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 172.52, 68.80, 62.41, 51.00, 35.25, 21.30, 17.70, 12.96; IR: 2874, 2094, 1733, 1443, 1278, 1094, 558 cm^{-1}.

Table 3 Energy values of GAP and poly(GA-carboxylate) compounds (**2**, **7**)

	GAP	Poly(GA$_{0.8}$-butyrate$_{0.2}$)	Poly(GA$_{0.8}$-decanoate$_{0.2}$)
Formula (repeating unit)	$C_3H_5N_3O$	$C_{3.8}H_{6.4}N_{2.4}O_{1.4}$	$C_{5.0}H_{8.8}N_{2.4}O_{1.4}$
FW (repeating unit)[g mol^{-1}]	99.09	108.11	124.94
$-\Delta U_{\mathrm{comb}}$ [J g^{-1}]	20 494	21 568	23 811
$-\Delta H_{\mathrm{comb}}$ [kJ mol^{-1}]	2029	2331	2976
$\Delta_f H^o_m$ [kJ mol^{-1}]	132	−81	−253
$\Delta_f H^o$ [kJ g^{-1}]	1.33	−0.75	−2.02

Table 4 Friction and impact sensitivity of poly(GA-carboxylate) compounds (**1–3**, **7**)

	Poly(GA$_{0.68}$-butyrate$_{0.32}$) (**1**)	Poly(GA$_{0.83}$-butyrate$_{0.17}$) (**2**)	Poly(GA$_{0.93}$-butyrate$_{0.07}$) (**3**)	Poly(GA$_{0.81}$-decanoate$_{0.19}$) (**7**)	GAP
Friction sensitivity (N)	>360	>360	>360	>360	>360
Impact sensitivity (J)	>50	>50	>50	>50	50

Poly(GA$_{0.9}$-butyrate$_{0.1}$) (3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.14, 78.60, 71.77, 70.60, 69.38, 51.57. 35.82, 18.29, 13.53; IR: 2874, 2092, 1733, 1443, 1277, 1096, 556 cm^{-1}.

Poly(GA$_{0.8}$-2-ethyl hexanoate$_{0.2}$) (4). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 175.63, 78.33, 69.54, 69.36, 69.12, 51.33, 46.82, 31.26, 29.17, 25.03, 22.22, 13.57, 11.45; IR: 2929, 2873, 2093, 1730, 1444, 1277, 1094, 556 cm^{-1}.

Poly(GA$_{0.8}$-octanoate$_{0.2}$) (5). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.27, 78.43, 69.20, 60.12, 51.41, 33.85, 31.36, 28.79, 28.63, 24.62, 22.31, 13.80; IR: 2925, 2871, 2093, 1734, 1443, 1277, 1103, 556 cm^{-1}.

Poly(GA$_{0.8}$-isononanoate$_{0.2}$) (6). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 172.49, 78.36, 69.59, 51.29, 50.10, 43.40, 30.70, 29.58, 29.58, 29.58, 26.61, 22.28; IR: 2931, 2871, 2093, 1732, 1442, 1276, 1078, 556 cm^{-1}.

Poly(GA$_{0.8}$-decanoate$_{0.2}$) (7). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 173.18, 78.34, 69.99, 69.14, 52.80, 51.31, 33.75, 31.46, 29.03, 28.86, 28.86, 28.74, 24.54, 22.28, 13.74.; IR: 2924, 2858, 2093, 1734, 1442, 1277, 1107, 556 cm^{-1}.

4. Conclusion

Poly(GA-carboxylate) compounds (**1–7**) were synthesized *via* the simultaneous substitution reaction with PECH, a quantitative amount of sodium azide, and sodium carboxylate in DMSO. The synthesized poly(GA-carboxylate) compounds (**1–7**) were characterized by FT-IR and ^{13}C NMR. The molecular composition of poly(GA-carboxylate) compounds (**1–7**) was confirmed by inverse gated decoupling ^{13}C NMR, and the average molecular weight was measured by GPC. The poly(GA-carboxylate) compounds (**1–7**) were observed to have molecular compositions similar to those theoretically calculated. The thermal properties were measured by DSC and TGA. The energy properties were determined in terms of the sensitivity and heats of combustion and formation. Poly(GA$_{0.8}$-butyrate$_{0.2}$) compound (**2**) and poly(GA$_{0.8}$-decanoate$_{0.2}$) compound (**7**) have negative formation enthalpies and higher heats of combustion than GAP. The viscosities and glass transition temperatures of poly(GA-carboxylate) compounds (**1–7**) were reduced in comparison to those of GAP. Moreover, the impact sensitivities of poly(GA-carboxylate) compounds (**1–3**, **7**) were lower than those of GAP. Consequently, poly(GA-carboxylate) compounds (**1–7**) exhibited better properties in comparison to GAP as a polymeric binder for solid propellants in terms of their energy and thermal properties. These properties are highly beneficial for their application and processing.

Our research group shall therefore select some poly(GA-carboxylate) and investigate the preparation of energetic thermoplastic elastomers (ETPE) using the selected poly(GA-carboxylate). This work will be presented in due course.

Conflicts of interest

There are no conflicts to declare.

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