



Investigation of ethylene-propylene based aliphatic polyketone thermal pyrolysis

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ABSTRACT

Aliphatic alternating ethylene-propylene-carbon monoxide (E-P-CO) polyketone is a recently commercialized engineering thermoplastic with promising material properties; however, its thermochemical conversion behavior under inert conditions has not yet been investigated. In this study, the pyrolysis of E-P-CO polyketone was examined in a laboratory-scale batch reactor, and product yields and compositions were determined. The pyrolysis resulted in 44.3 wt% liquid, 34.4 wt% solid residue, and 21.3 wt% gaseous products. Gas analysis revealed high concentrations of CO in the early stage of the process, followed by increasing methane, hydrogen, and light hydrocarbons as the reaction progressed. The heating value of the gas fraction increased from 17.1 to 33.8 MJ/m³, indicating potential energetic utilization. Distillation and GC-MS analysis of the light oil fraction (20–210 °C) identified ketones, cyclopentenones, furans, and aromatic compounds as dominant products. These results were further supported by FTIR analysis. The formation of cyclopentenone derivatives confirms that intramolecular cyclization reactions represent a major degradation pathway, similarly to ethylene-carbon monoxide polyketones.

1. Introduction

Aliphatic alternating ethylene-propylene-carbon monoxide (E-P-CO) polyketone (PK) (e.g., Hyosung POKETONE™) is a relatively new engineering thermoplastic with excellent mechanical, chemical, and barrier properties, used in automotive, packaging, and industrial components [1]. It was synthesized using a palladium-based catalyst system and scaled up for industrial production in 2019, which is a notable milestone [2]. The material itself consists of a perfectly alternating olefin and carbon monoxide, offering a unique combination of performance and processing properties.

Although polyketones have attracted increasing attention owing to their unique properties [3], given the relative novelty of the E-P-CO PK material, several aspects of the material's properties have not yet been investigated, including the thermochemical behavior, i.e. pyrolysis. Pyrolysis involves the thermal decomposition of polymers at elevated temperatures in the absence of oxygen, producing gaseous, liquid, and solid products [4]. The composition of pyrolysis products strongly depends on the chemical structure of the polymer backbone, as well as on the reaction conditions and reactor configuration. During thermal degradation, polymer chains undergo random scission reactions that

generate smaller molecules such as hydrocarbons, oxygenated compounds, and other low-molecular-weight fragments.

Belov and Novikova published a study reviewing the characteristic features of different polyketones, including their catalytic synthesis. The review includes a detailed description of CO-ethylene, CO copolymers with propylene and higher olefins, CO-cyclic olefins, CO-functional α -olefins and other monomers, CO-linear dienes, CO-cyclic dienes, CO-allene derivatives, and copolymers of CO with styrene and its derivatives [5]. Chiantore et al. [6] investigated the thermal degradation of ethylene-carbon monoxide (E-CO) alternating copolymers, which is probably the closest polymer structure to E-P-CO type PK. They found that the E-CO PK degradation mechanism occurs not only through chain scission and fragmentation but also through extensive intramolecular cyclization reactions, resulting in the formation of cyclopentenone, furanic, and aromatic structures, along with water production. The authors also propose the thermal degradation mechanism of E-CO PK. Cyclization and dehydration mechanisms were also observed for the same material by Chien et al. [7], who reported carbonaceous residues between 20 and 30%. Xiao et al. [8] concluded that while alternating E-CO PKs have a high melting point and insolubility, the material without a perfect alternating structure has better processability. Cho et al. [9]

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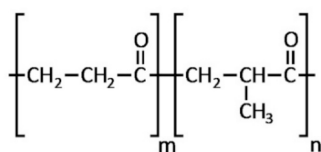


Fig. 1. The structure of aliphatic polyketone used in this study.

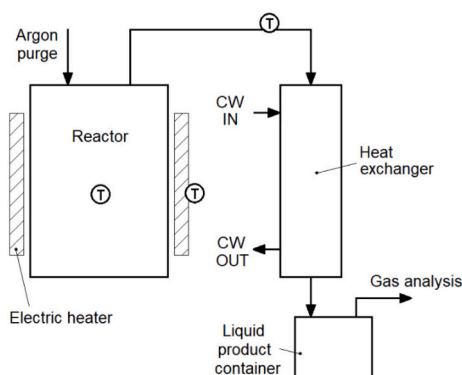


Fig. 2. Schematic illustration of the pyrolysis system (CW - cooling water, T - temperature measurement points).

described the *E*-CO PK as a first-generation PK with a high melting temperature (255–260 °C) but also highlighted its disadvantages, including brittleness, stiffness, and poor processability. *E*-P-CO PK was described as the latest-generation PK, in which adding a propylene monomer to the *E*-CO PK backbone helps compensate for the aforementioned disadvantages. In this study, thermogravimetric analyses of *E*-P-CO PK were performed for material description; however, the authors used air flow, so it cannot be considered pyrolysis. Lin et al. [10] investigated the hygrothermal conditioning on the chemical, thermal, and mechanical properties of *E*-P-CO PK. Thermogravimetric measurement showed that the degradation starts at around 410 °C for virgin *E*-P-CO PK, while the maximum degradation rate occurred at around 440 °C. However, the atmosphere used for obtaining the thermogravimetric data nor the derivatograms are not provided. Mu et al. [11] created a different polymer structure by copolymerizing styrene and carbon monoxide (Sty-CO), and investigated the thermal degradation mechanism. Thermogravimetric analysis showed a one-step degradation mechanism at 387–396 °C at a 10 K/min heating rate. Additionally, solid residue is estimated to be 6–8 wt% based on TG plots, which is significantly lower than that of *E*-CO PK. Another thermal degradation study was published by Bertini et al. [12] regarding Sty-CO PK. Based on TG analysis, the solid residue was 3.5 wt% at 700 °C, and the main

degradation products were styrene (60.4 wt%), ethylbenzene (17.2 wt%), toluene (7.7 wt%), and carbon monoxide.

The literature indicates that *E*-P-CO PK (Poketone) is gaining attention, but investigations typically focus on production or material properties. To the best of the author's knowledge, the pyrolysis behavior and product distribution of aliphatic polyketone (POKETONE™) have not yet been reported. Understanding the thermochemical degradation of this emerging engineering polymer is essential for evaluating its potential recycling routes and energy recovery options. Therefore, the objective of the present work was to investigate the pyrolysis behavior of an *E*-P-CO polyketone using a laboratory-scale pyrolysis reactor. The liquid pyrolysis products were further separated by distillation and analyzed by gas chromatography–mass spectrometry (GC–MS) and FTIR in order to identify the main compounds formed during thermal decomposition. The results provide new insights into the degradation pathways and product distribution of this latest generation aliphatic polyketone.

2. Materials and methods

Aliphatic polyketone (*E*-P-CO PK) (Fig. 1) was pyrolyzed in an electrically heated lab-scale batch reactor filled with 250 g of material. Pyrolysis vapors were condensed in a water-cooled heat exchanger, while the non-condensable gases were directed to a flare. Gas samples were collected from the pyrogas stream during the pyrolysis process and analyzed using gas chromatography (models: Dani Master with a FID detector and a Rt-Alumina BOND/Na₂SO₄ 30 m × 0.53 mm × 10 μm column for light hydrocarbons, and Agilent 490 MicroGC with TCD detector and CP-COx column for CO₂, CO, and H₂ analyses). Prior to and following each pyrolysis run, the system was purged with argon for 10 min to remove air and residual vapors, respectively. The pyrolysis process started at ambient temperature and ended when the reactor's temperature exceeded 500 °C. A schematic illustration of the pyrolysis system is presented in Fig. 2. The maximum standard deviation of the pyrolysis oil recovery and solid residue yields was 1.0 wt%, based on prior measurements performed using the same experimental setup.

The ultimate analysis of the PK was performed with a Carlo Erba EA 1108 elemental analyzer following EN ISO 16948:2015 and MSZ 24051:2001 standard methods. The carbon and hydrogen content were 64.43 wt% and 7.45 wt%, respectively. Nitrogen and sulfur were below the detection limit, being less than 0.4 wt% and 0.2 wt%, respectively. Thermogravimetric analysis was performed using a MOM Derivatograph C/PC instrument in a nitrogen atmosphere at a heating rate of 10 °C/min. Fig. 3 shows the results. The higher heating value (HHV) of the PK was 27.94 MJ/kg, determined according to EN 14918:2009 using an isoperibol bomb calorimeter (Parr 6200). The plastic was used “as received,” in pellet form, with a typical particle size of ≈5 mm.

The pyro-oil was further processed by atmospheric distillation to

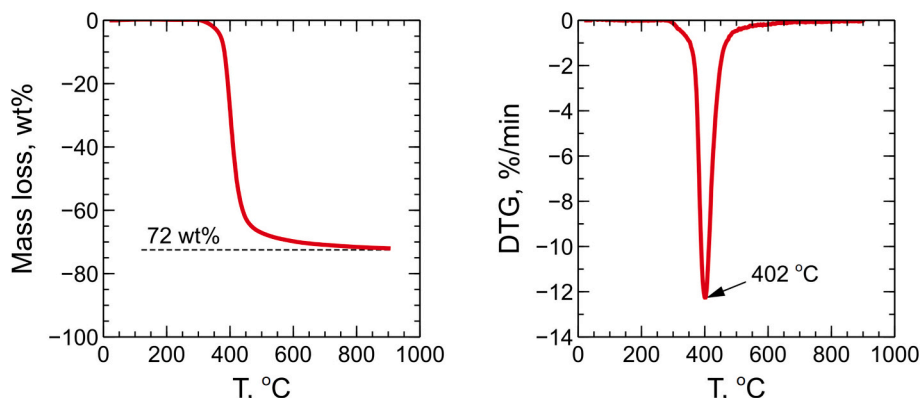


Fig. 3. Thermogravimetric analysis of *E*-P-CO type PK utilized in this study.

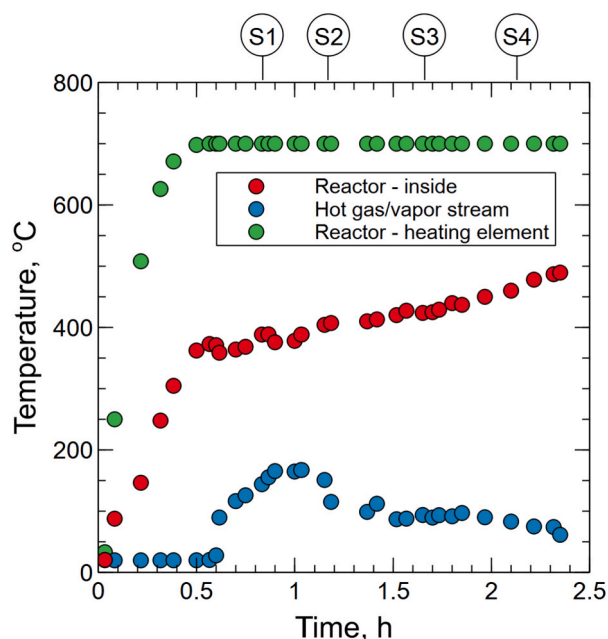


Fig. 4. Reactor inside, hot gas/vapor, and heating element temperatures as a function of time. Gas sampling points are indicated as S1–S4.

Table 1
Mass balance results of the pyrolysis run with E-P-CO PK.

	Mass, g	Concentration, wt%
Feedstock	250	–
Pyrooil	110.7	44.3
Solid residue	86.0	34.4
Pyrogas	53.3	21.3

obtain the light fraction (20–210 °C), which was analyzed by FTIR (model: Bruker Tensor 27) and GC–MS (model: Agilent 6890/5973, columns: DB-5 30 m × 0.25 mm × 0.25 μm and DB-VRX 60 m × 0.32 mm × 1.4 μm) to evaluate the molecular composition. Molecules with a match factor of at least 80% were considered and evaluated during GC–MS analysis. The distillation was performed in a traditional laboratory spherical glass retort placed in a heating mantle. Vapor condensation was ensured by a water-cooled Liebig condenser.

3. Results

Fig. 4 shows the main temperature profiles of the reactor interior, hot gas/vapor stream, and heating element as a function of process time, together with the gas sampling time points (S1–S4). The hydrocarbon vapors leaving the reactor reach a maximum temperature of ≈185 °C after approximately 1 h, corresponding to the period of the highest degradation rate and, consequently, the greatest hydrocarbon vapor production. At this stage, the temperature inside the reactor is approximately 400 °C, which is in good agreement with the thermogravimetric analysis results presented in Fig. 3.

The mass balance of the pyrolysis is summarized in Table 1. A total of 250 g of PK feedstock was charged to the reactor, yielding 44.3 wt% liquid product, 34.4 wt% solid residue, and 21.3 wt% gaseous products. The proportion of solid residue is consistent with the previously presented thermogravimetric results, where 67.1 wt% mass loss (i.e. 32.9 wt% solid residue) was measured at 500 °C. The relatively high solid residue represents a notably high value even within oxygen-containing plastic materials such as polyethylene terephthalate (23.6 wt%) [13].

Four gas samples were collected from the pyrogas at different times during the experiment (Fig. 4). These samples were analyzed by a gas

Table 2
Composition of the pyrolysis gas.

Formula	Name	Concentration, vol%			
		Sample 1	Sample 2	Sample 3	Sample 4
CH ₄	Methane	6.5	23.9	39.3	34.4
C ₂ H ₆	Ethane	5.6	8.9	12.6	11.1
C ₂ H ₄	Ethene	1.8	2.0	2.4	1.2
C ₃ H ₆	Propene	0.6	1.0	1.3	1.1
C ₃ H ₈	Propane	0.9	1.9	3.2	1.4
H ₂	Hydrogen	0.8	3.4	15.2	29.5
CO	Carbon-monoxide	65.8	48.8	17.2	14.6
CO ₂	Carbon dioxide	5.5	7.1	3.0	1.2
	Other	12.5	3.0	5.8	5.5

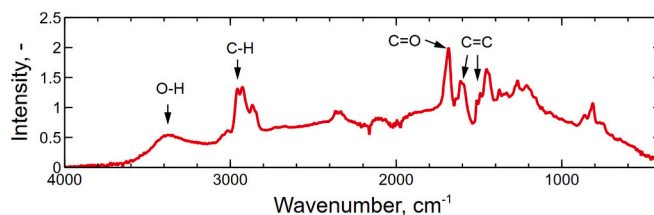


Fig. 5. FTIR spectrum of the solid residue.

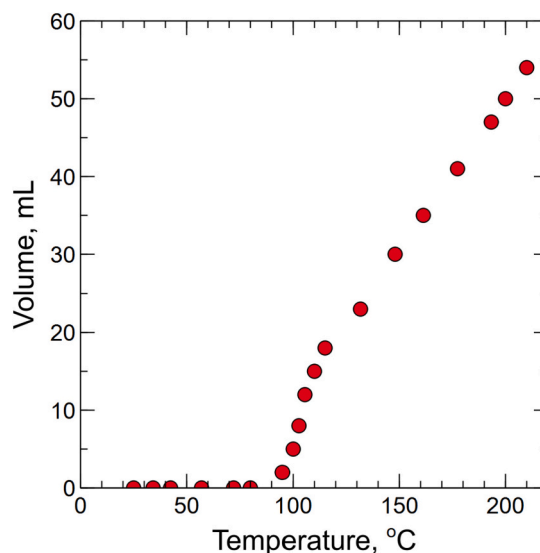


Fig. 6. Distillation curve for the light fraction of the pyrooil.

chromatograph after pyrolysis. The results are summarized in Table 2. Based on the data presented, the hydrogen and hydrocarbon content of the pyrogas increases as the pyrolysis process progresses, while the concentrations of carbon monoxide and carbon dioxide decrease. The presence of CO and CO₂ indicates that the oxygen atoms in the molecular structure also participate in the reactions; however, their contribution becomes less significant as the process proceeds. Sample S4 exhibited an elevated hydrogen concentration of 29.5 vol%, accompanied by a relatively lower hydrocarbon content. The HHV of the gases was calculated by summing the individual heating values of the components, weighted by their concentrations. Samples 1, 2, 3, and 4 yielded HHV values of 17.1 MJ/m³, 25.9 MJ/m³, 33.8 MJ/m³, and 29.7 MJ/m³, respectively, considered significant for energetic utilization through combustion.

The elemental composition and HHV of the solid residue were determined using the same instruments as for the feedstock analysis. The carbon and hydrogen content were 90.13 wt% and 4.11 wt%, respectively. Nitrogen and sulfur were below the detection limit, being less

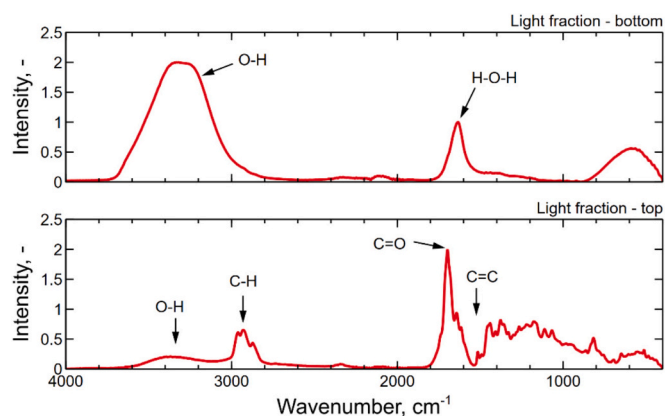


Fig. 7. FTIR spectra of the light liquid fractions (20–210 °C) from distillation.

than 0.4 wt% and 0.2 wt%, respectively. Additionally, the HHV of the solid residue is consistent with its high carbon content, at 35.18 MJ/kg. The presence of hydrogen in the solid residue indicates that some hydrocarbons are also present which is supported by FTIR measurement seen in Fig. 5. The FTIR spectrum of the solid residue exhibited a broad O—H stretching band around 3400 cm^{-1} and aliphatic C—H stretching vibrations at $2950\text{--}2850\text{ cm}^{-1}$. An absorption band at $\approx 1700\text{ cm}^{-1}$

indicated the presence of carbonyl groups, while bands at ~ 1600 and $\sim 1520\text{ cm}^{-1}$ were assigned to aromatic/conjugated C=C vibrations, and also suggesting the formation of PAH-like structures during pyrolysis. The elevated broadband baseline is characteristic of a highly carbonized coke-like residue, containing residual oxygenated and hydrogen-containing functionalities.

The light fraction (20–210 °C) of the pyrooil consisted of two independent immiscible phases. The bottom one is a water-based solution with only 6.6 wt% identified hydrocarbon content by GC–MS. The distillation curve is shown in Fig. 6, from which the water fraction is estimated to be around $\approx 27\text{ vol\%}$. The most abundant hydrocarbons were 2,3-dimethyl-2-cyclopenten-1-one (2.09 wt%), 3-methyl-2-cyclopenten-1-one (0.78 wt%), and 3,6-heptanedione (0.65 wt%). The dominant presence of water was indicated by FTIR measurements shown in Fig. 7.

The ten most abundant components in the upper part of the light fraction are summarized in Table 3. Similar to E-CO PK pyrolysis, cyclization reactions also occur during E-P-CO PK pyrolysis, resulting in the formation of cyclopentenone, furanic, and aromatic structures. However, a smaller part of the cracking remains as chain fragments, including acetone, 2-butanone, 3-pentanone, and 3,6-heptanedione. Additionally, bicyclic and even tricyclic hydrocarbons were identified with concentrations of 3.26 wt% and 0.05 wt%, respectively. The list of all identified components in this fraction and their concentrations is listed in Table S1. The concentration of oxygen-containing compounds is

Table 3

Summary of the ten most abundant compounds identified during GC–MS analysis in the upper part of the light fraction.

No.	Name	Structure	Formula	Concentration, wt%
1	Acetone		C ₃ H ₆ O	2.58
2	2-Butanone		C ₄ H ₈ O	1.32
3	3-Pentanone		C ₅ H ₁₀ O	1.66
4	Furan, 2,5-dimethyl-		C ₆ H ₈ O	1.31
5	Furan, 2-ethyl-5-methyl-		C ₇ H ₁₀ O	2.64
6	1,2,4,4-Tetramethylcyclopentene		C ₉ H ₁₆	1.93
7	3,6-Heptanedione		C ₇ H ₁₂ O ₂	1.34
8	2-Cyclopenten-1-one, 2,3-dimethyl-		C ₇ H ₁₀ O	7.54
9	2-Cyclopenten-1-one, 2,3,4-trimethyl-		C ₈ H ₁₂ O	7.43
10	Phenol, 4-methyl-		C ₇ H ₈ O	1.05

high, and no dominant component can be identified in the light oil fraction. The total amount of light fraction from the distillation was 567 g/kg_{oil} or 251 g/kg_{PK}.

The GC–MS results are further supported by FTIR measurement seen in Fig. 7 (bottom plot). Well-defined absorption bands in the 2950–2850 cm^{−1} region correspond to aliphatic C–H stretching vibrations, indicating a significant hydrocarbon content. A strong and sharp absorption band centered at approximately 1710 cm^{−1} is assigned to the C=O stretching vibration of ketone groups, which is in excellent agreement with the GC–MS identification of acetone, butanone, pentanone, and cyclopentenone derivatives. Additional absorption bands in the 1600–1500 cm^{−1} region are attributed to C=C stretching vibrations, suggesting the presence of conjugated and aromatic structures. The most distinctive feature of the spectrum is the complex and structured absorption pattern observed between 1200 and 1000 cm^{−1}, which represents a characteristic organic fingerprint region. These bands are associated with C–O stretching vibrations of oxygen-containing cyclic compounds, including furanic and cyclopentenone-type structures. The coexistence of carbonyl, unsaturated, and C–O-containing functional groups indicates that the organic phase is composed of both chain-scission fragments and cyclized degradation products.

4. Conclusions

The pyrolysis behavior of an ethylene–propylene–carbon monoxide aliphatic polyketone was investigated in a laboratory-scale batch reactor. The process yielded 44.3 wt% liquid products, 21.3 wt% gases, and a relatively high solid residue of 34.4 wt%, indicating extensive char formation during thermal degradation. Gas analysis revealed an initial dominance of CO and CO₂ followed by increasing methane, hydrogen, and light hydrocarbons. The HHV of the gas fraction increased significantly during the process, suggesting potential for energetic utilization. GC–MS analysis of the distilled oil fraction identified ketones, cyclopentenones, furans, and aromatic compounds as major products, confirming that intramolecular cyclization reactions represent a key degradation pathway along with water production. These findings provide the first experimental insight into the thermochemical decomposition of E-P-CO polyketone and may support the development of recycling strategies for this emerging engineering polymer.

CRedit authorship contribution statement

Zsolt Dobó: Writing – review & editing, Writing – original draft, Visualization, Supervision, Investigation, Data curation. **Helga Kovács:** Writing – review & editing, Validation, Resources, Formal analysis. **Annamária Polyákné Kovács:** Writing – review & editing, Writing – original draft, Validation, Resources, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuproc.2026.108528>.

Data availability

Data will be made available on request.

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