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Explora: Environment and Resource

ORIGINAL RESEARCH ARTICLE

Synergistic effects and mechanism of hazardous chlorinated aromatic hydrocarbon formation during plastics combustion: A multiscale study

Supplementary Files

1. Theory and interpretations of two-dimensional correlation spectroscopy maps

Two-dimensional correlation spectroscopy (2D-COS) is a powerful analytical technique that utilizes mathematical correlation analysis to expand dynamically perturbed spectral data into a second dimension, thereby significantly enhancing spectral resolution and revealing interrelationships and interactions among functional groups. By applying an external perturbation (e.g., temperature, time, concentration, or stress) to the system, a set of dynamic spectra is generated and subsequently converted into synchronous [$\Phi(\nu_1, \nu_2)$] and asynchronous [$\Psi(\nu_1, \nu_2)$] correlation maps.[1,2] In the synchronous spectrum, auto-peaks represent the overall sensitivity of spectral intensity at a given wavenumber to the external perturbation. The sign (positive or negative) of cross-peaks indicates whether intensity changes at two different wavenumbers occur synchronously (in the same direction) or asynchronously (in opposite directions), respectively, suggesting potential chemical coupling or coordinated responses to the perturbation.[3,4] In contrast, the asynchronous spectrum effectively resolves overlapped peaks present in one-dimensional spectra and provides insights into the sequential order of functional group responses via the sign of its cross-peaks and Noda's rules.[5] This facilitates a detailed mechanistic understanding of dynamic structural changes and intermolecular interactions in complex systems, including polymers, proteins, and chemical reaction processes.

The core mathematical expression is based on the definition of the dynamic spectrum $\tilde{y}(\nu, d)$, and its calculation is expressed as Equation S1:

$$\tilde{y}(\nu, d) = \begin{cases} y(\nu, d) - \bar{y}(\nu) & 1 \le d \le T \\ 0 & \text{otherwise} \end{cases} \tag{S1}$$

here, $\tilde{y}(\nu, d)$ represents the spectral intensity measured for the system at the wave number under the influence of an external perturbation d (such as temperature, time, concentration, etc.). $\bar{y}(\nu)$ denotes the reference spectrum, which is typically defined as the average spectral intensity over the entire perturbation range, as shown in Equation S2:

$$\bar{y}(\nu) = \frac{1}{T}\sum_{j=1}^{T} y(\nu, d_j) \tag{S2}$$

On this basis, the generalized two-dimensional synchronous Φ (ν1, ν2) and asynchronous Ψ (ν1, ν2) correlation spectra are calculated as Equations S3 and S4:

$$\Phi(\nu_1, \nu_2) = \frac{1}{T-1}\sum_{j=1}^{T} \tilde{y}_j(\nu_1) \cdot \tilde{y}_j(\nu_2) \tag{S3}$$

$$\Psi(\nu_1, \nu_2) = \frac{1}{T-1}\sum_{j=1}^{T} \tilde{y}_j(\nu_1) \cdot \sum_{k=1}^{T} N_{jk}\tilde{y}_k(\nu_2) \tag{S4}$$

In these equations, N_{jk} is an element of the Hilbert–Noda transformation matrix, defined as Equation S5:

$$N_{jk} = \begin{cases} 0 & \text{if } j = k \\ \dfrac{1}{\pi(k-j)} & \text{if } j \ne k \end{cases} \tag{S5}$$

The synchronous spectrum $\Phi(\nu_1, \nu_2)$ characterizes the similarity of spectral intensity changes at two different wave numbers ν_1 and ν_2, indicating simultaneous responses to the perturbation. The asynchronous spectrum $\Psi(\nu_1, \nu_2)$, in

contrast, characterizes the difference in the sequential order of these intensity changes.

Furthermore, in the two-dimensional correlation spectroscopy of moving windows (MW2D-COS) analysis, the concept of perturbation-related is often introduced. The synchronous and asynchronous spectra are respectively similar to the first-order and second-order derivatives of the perturbation in the original dynamic spectral data, and can be mathematically approximated as Equations S6 and S7:

$$\Phi_{\mathrm{MW}}(\nu,d) \approx \frac{\partial \tilde{y}(\nu,d)}{\partial d} \tag{S6}$$

$$\Psi_{\mathrm{MW}}(\nu,d) \approx -\frac{\partial^2 \tilde{y}(\nu,d)}{\partial d^2} \tag{S7}$$

This theoretical framework enables 2D-COS to decipher complex interactions in systems such as polymers, biological tissues, and chemical reactions.[6]

By performing 2D-COS analysis on spectral sequences obtained from thermogravimetry–infrared spectroscopy analysis (gas phase) and *in situ* infrared spectroscopy (solid phase), respectively, this approach surpasses the limitations of conventional one-dimensional spectroscopy. For gaseous volatiles, 2D-COS analysis of the Fourier transform infrared spectroscopy spectral sequence from thermogravimetry–infrared spectroscopy analysis uses temperature as the external perturbation variable. This enables the asynchronous spectrum to precisely identify the sequential order of intensity changes in the characteristic absorption peaks of various volatile organic compounds (VOCs). Thus, it determines their temporal release sequence. For solid residues, 2D-COS analysis of *in situ* infrared spectroscopy–Fourier transform infrared spectroscopy spectra acquired at different temperatures or time points allows inference of the evolution and transformation mechanisms of various functional groups during polymer thermal degradation. This is achieved by examining synchronous and asynchronous spectra. Furthermore, hetero-spectral 2D-COS correlates one set of spectral sequences with another. It can reveal sequential correlations between gaseous and solid phases. The appearance of a significant cross-peak between a specific gaseous VOC absorption peak and a solid functional group absorption peak in the generated heterospectral asynchronous 2D-COS map can be interpreted using Noda's rules based on the sign of the cross-peak. This indicates whether cleavage or modification of a specific functional group in the solid precedes the release of a specific VOC, or vice versa. This provides direct spectroscopic evidence for elucidating the detailed chemical mechanisms of plastic combustion.

2. Details of the kinetics analysis

For the solid-phase combustion reaction, the reaction rate can be expressed as Equation S8

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \tag{S8}$$

where α represents the conversion rate of coal and biomass at a specific temperature (%); t is the reaction time; T is the thermodynamic temperature (K); $k(T)$ is the reaction constant; and $f(\alpha)$ is the reaction mechanism function.

α can be expressed as Equation S9:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_{\mathrm{f}}} \tag{S9}$$

where m_0, m_t, and m_{f} represent the mass of the sample at the beginning of the experiment, at time t, and at the end of the experiment, respectively.

According to the Arrhenius equation, the relationship between the reaction rate constant $k(T)$ and the thermodynamic T can be expressed as Equation S10:

$$k(T) = A \exp\left(-\frac{E_\alpha}{RT}\right) \tag{S10}$$

where A is the pre-exponential factor (s^{-1}); E_α is the activation energy (J/mol); and R is the gas constant (8.314 J/mol·K).

In the process of non-isothermal combustion, the temperature T is a linear function of time t. The heating rate β can be expressed in Equation S11, and consequently, Equation S8 can be transformed into Equation S12:

$$\beta = \frac{dT}{dt} = \text{const} \tag{S11}$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E_\alpha}{RT}\right)f(\alpha) \tag{S12}$$

If Equation S12 is rearranged and subjected to simultaneous integration at both ends, then Equation S12 can be rewritten as Equation S13:

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E_\alpha}{RT}\right)\mathrm{d}T \tag{S13}$$

The functional forms of f(α) and g(α) representing various reaction mechanisms are listed in **Table S6**. Various models can be employed to solve Equation S14 and determine the associated kinetic parameters. Following the recommendations of the International Confederation for Thermal Analysis and Calorimetry (ICTAC), the iso-conversational methods were adopted, as they enable a more reliable determination of the activation energy (E_α). Accordingly, three iso-conversional methods—Kissinger–Akahira–Sunose, Flynn–Wall–Ozawa, and Starink—were used to evaluate the E_α.

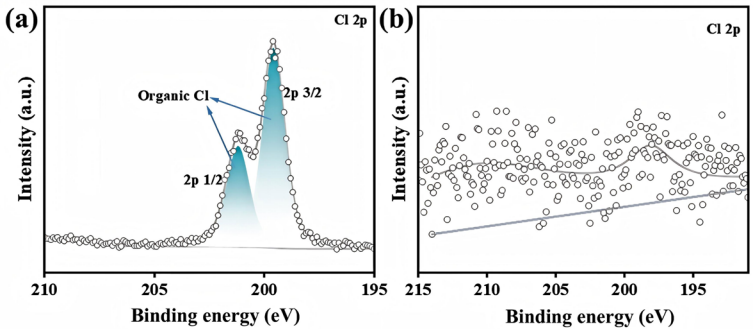

Figure S1. Polypropylene: polystyrene: polyvinyl chloride spectra of chlorine (Cl) 2p before and after combustion reaction. (a) Before the reaction. (b) After combustion from room temperature to 400 °C.

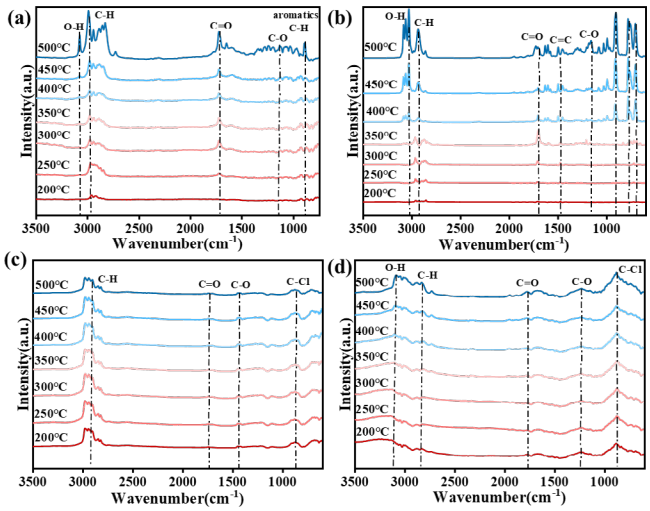

Figure S2. Fourier transform infrared spectroscopy spectra of residual solids at selected temperatures during combustion. (a) Polypropylene (PP). (b) Polystyrene (PS). (c) Polyvinyl chloride (PVC). (d) PP:PS:PVC.

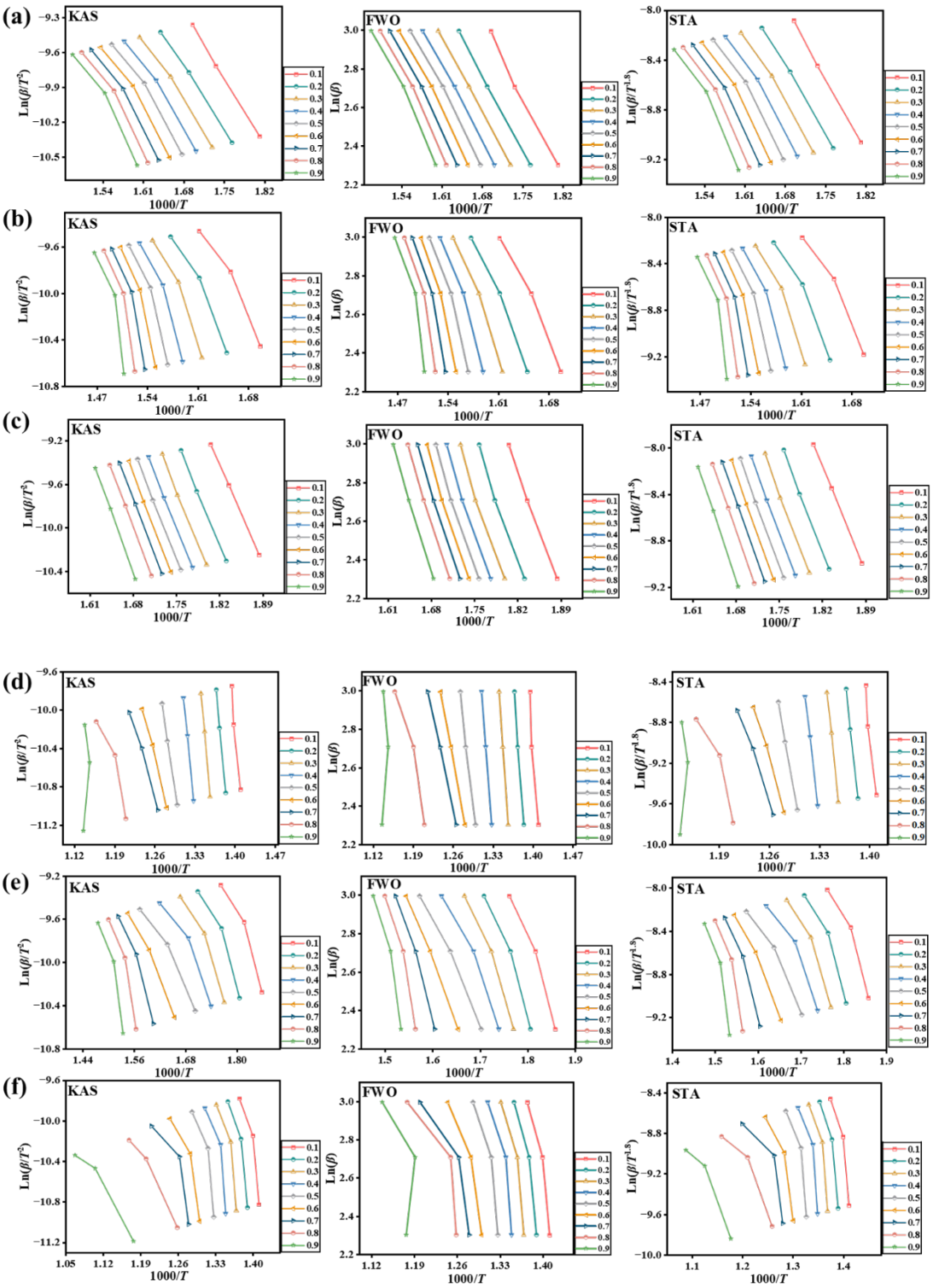

Figure S3. Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO), and Starink (STA) methods for calculating E_α values. (a) Polypropylene (PP). (b) Polystyrene (PS). (c) Polyvinyl chloride (PVC) dechlorination stage. (d) PVC residual carbon oxidation stage. (e) PP:PS:PVC dechlorination stage. (f) PP:PS:PVC residual carbon oxidation stage calculated at different conversion rates.

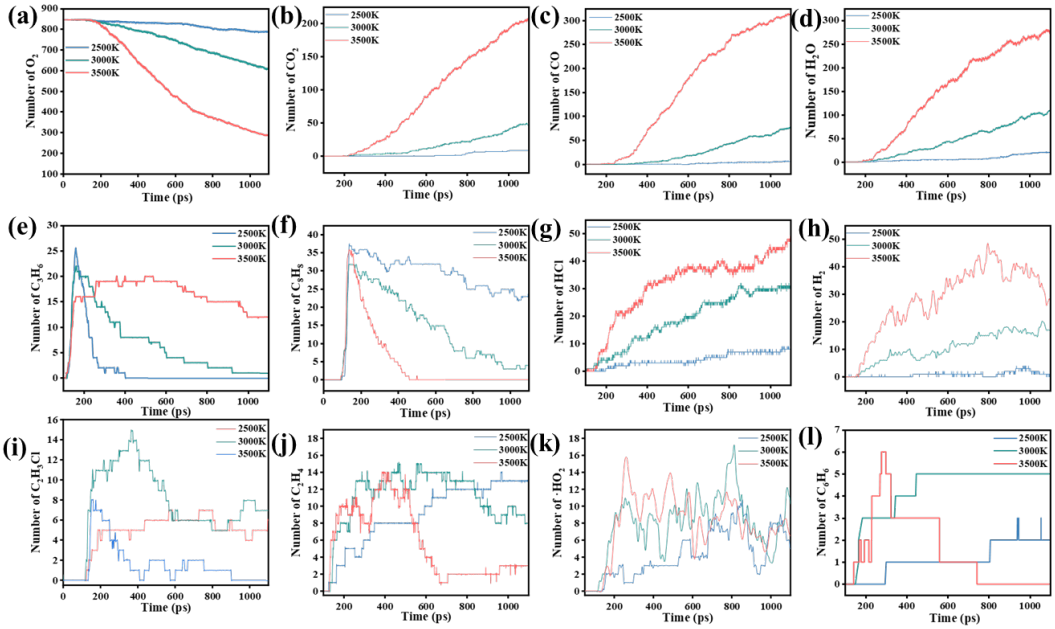

Figure S4. Cumulative changes of the simulation results based on the reactive force field molecular dynamics at different temperatures with respect to the constant temperature time. (a) Oxygen (O_2) consumption. (b) Carbon dioxide (CO_2) generation. (c) Carbon monoxide (CO) generation. (d) water (H_2O) generation. (e) Propylene (C_3H_6) generation. (f) Styrene (C_8H_8) generation. (g) Hydrogen chloride (HCl) generation. (h) Hydrogen (H_2) generation. (i) Vinyl chloride (C_2H_3Cl) generation. (j) Ethylene (C_2H_4) generation. (k) Hydroperoxyl radical ($\cdot HO_2$) generation. (l) Benzene (C_6H_6) generation.

Table S1. Compounds of plastics identified from headspace gas chromatography–mass spectrometry

Compound	Chemical formula	RT	CAS	Score	RI_{lib}	RI_{exp}
PP						
Propiolactone	$C_3H_4O_2$	2.448	57–57–8	83.150	705	724
Hexanoic acid	$C_6H_{12}O_2$	9.415	142–62–1	87.670	982	898
2,4-Dimethyl-1-heptene	C_9H_{18}	10.15	14,549– 87–2	93.630	897	915
2,4-Dimethyl-1-heptene	C_9H_{18}	10.222	14,549–87–2	93.360	897	922
Heptanoic acid	$C_7H_{14}O_2$	13.405	111–14–8	82.320	1,078	1,090
Z-8-Methyl-9-tetra decenoic acid	$C_{15}H_{28}O_2$	14.085	1,000,130–84–5	82.560	1,840	1,808
1-Hexadecanol,2-methyl-	$C_{17}H_{36}O$	15.228	2,490–48–4	82.070	1,890	1,923
1-Hexadecanol,2-methyl-	$C_{17}H_{36}O$	15.299	2,490–48–4	81.090	1,890	1,930
Oleic acid	$C_{18}H_{34}O_2$	15.648	112–80–1	81.270	2,095	1,965

(Cont'd...)

Table S1. *Continued*

Compound	Chemical formula	RT	CAS	Score	RI_{lib}	RI_{exp}
Oleic acid	$C_{18}H_{34}O_2$	16.13	112–80–1	84.590	2,095	2,013
Octadecanoic acid,4-hydroxy-,methylester	$C_{19}H_{38}O_3$	16.5	2,420–38–4	80.150	2,239	2,060
Oleic acid	$C_{18}H_{34}O_2$	17.075	112–80–1	82.170	2,174	2,208
Oleic acid	$C_{18}H_{34}O_2$	17.403	112–80–1	83.120	2,174	2,241
E,E,Z-1,3,12-Nonadecatriene-5,14-diol	$C_{19}H_{34}O_2$	18.528	1,000,131–11–4	81.620	2,029	2,360
E,E,Z-1,3,12-Nonadecatriene-5,14-diol	$C_{19}H_{34}O_2$	19.074	1,000,131–11–4	83.540	2,029	2,376
Oleic acid	$C_{18}H_{34}O_2$	19.784	112–80–1	84.020	2,174	2,387
Perhydroindene-4-carboxylic acid, 6-acetoxy-2,3-epoxy-1,1-epoxymethyl-3a_x0002_hydroxy-5-isopropenyl-7a_x0002_methyl-7-oxo-, methyl ester	$C_{18}H_{22}O_8$	20.859	1,000,194–01–0	82.200	2,270	2,420
Perhydroindene-4-carboxylic acid, 6-acetoxy-2,3-epoxy-1,1-epoxymethyl-3a_x0002_hydroxy-5-isopropenyl-7a_x0002_methyl-7-oxo-, methyl ester	$C_{18}H_{22}O_8$	21.212	1,000,194–01–0	81.310	2,270	2,470
E,E,Z-1,3,12-Nonadecatriene-5,14-diol	$C_{19}H_{34}O_2$	22.014	1,000,131–11–4	81.950	2,029	2,514
PS						
Benzene	C_6H_6	4.488	71–43–2	72.230	680	650
Ethane,1,1-diethoxy-	$C_6H_{14}O_2$	7.205	105–57–7	90.750	722	750
Heptane,3-methylene-	C_8H_{16}	8.556	1,632–16–2	79.120	785	780
Propanoicacid,2-hydroxy-,ethyl ester	$C_5H_{10}O_3$	10.056	97–64–3	84.680	803	806
Phenylethyne	C_8H_6	11.347	536–74–3	83.690	868	885
Styrene	C_8H_8	11.63	100–42–5	87.040	883	910
Benzeneethanol, beta, -ethenyl-	$C_{10}H_{120}$	12.724	6,052–63–7	79.590	1,261	1,120
Benzeneethanol, beta, -ethenyl-	$C_{10}H_{120}$	14.551	6,052–63–7	74.250	1,261	1,255
Benzene,1-propynyl-	C_9H_8	14.713	673–32–5	86.320	1,038	1,272

(*Cont'd...*)

Table S1. *Continued*

Compound	Chemical formula	RT	CAS	Score	RI_{lib}	RI_{exp}
Tetracyclo[5,3,0,0<2,6>,0<3,10>]deca-4,8-diene	$C_{10}H_{10}$	16.775	3,4324–40–8	82.130	1,572	1,478
1-Dodecanol,3,7,11-trimethyl-	$C_{15}H_{32}O$	17.028	6,750–34–1	78.260	1,566	1,503
Naphthalene	$C_{10}H_{8}$	17.097	91–20–3	85.000	1,098	1,510
7-Methyl-Z-tetradecen-1-ol acetate	$C_{17}H_{32}O_{2}$	17.376	1,000,130–99–6	70.260	2,171	2,040
7-Methyl-Z-tetradecen-1-ol acetate	$C_{17}H_{32}O_{2}$	18.227	1,000,130–99–6	75.250	2,171	2,123
PVC						
Dimethyl ether	$C_{2}H_{6}O$	4.894	115–10–6	81.870	327	309
Ethane,1,1-diethoxy-	$C_{6}H_{14}O_{2}$	7.148	105–57–7	86.200	714	693
1-Heptene,2-methyl-	$C_{8}H_{16}$	8.526	15,870–10–7	78.770	696	712
Octane,4-methyl-	$C_{9}H_{20}$	9.550	2,216–34–4	80.460	865	855
2,4-Dimethyl-1-heptene	$C_{9}H_{18}$	10.126	19,549–87–2	95.260	897	912
Cyclopentane, 1,2,3,4,5-pentamethyl-	$C_{10}H_{20}$	11.486	1,000,152–79–7	81.660	944	949
2-Heptanone,4-methyl-	$C_{8}H_{16}O$	12.585	6,137–06–0	85.870	934	957
Nonane, 4-methyl-	$C_{10}H_{22}$	13.003	17,301–94–9	82.510	944	964
Octane, 3,3-dimethyl-	$C_{10}H_{22}$	13.971	4,110–44–5	76.910	944	971
Dodecane,4,6-dimethyl-	$C_{14}H_{30}$	14.041	61,141–72–8	83.380	1,226	1,204
Dodecane,4,6-dimethyl-	$C_{14}H_{30}$	14.207	61,141–72–8	83.370	1,226	1,221
Cyclohexanone,4-(1,1-dimethylethyl)-	$C_{10}H_{180}$	14.442	98–53–3	76.340	1,208	1,244
6-Tridecene, (Z)-	$C_{13}H_{26}$	14.612	6,508–77–6	81.100	1,289	1,260
Dodecane,4,6-dimethyl-	$C_{14}H_{30}$	14.852	61,141–72–8	86.300	1,226	1,275
Dodecane,4,6-dimethyl-	$C_{14}H_{30}$	15.615	61,141–72–8	83.600	1,226	1,296

(*Cont'd...*)

Table S1. *Continued*

Compound	Chemical formula	RT	CAS	Score	RI_{lib}	RI_{exp}
Cyclopentane,1,2-dibutyl-	$C_{13}H_{26}$	16.047	62,199–52–4	82.640	1,289	1,305
1-Dodecanol,3,7,11-trimethyl-	$C_{15}H_{32}O$	16.151	6,750–34–1	80.130	1,566	1,520
Tetradecane,2,6,10-trimethyl-	$C_{17}H_{36}$	17.237	14,905–56–7	76.060	1,685	1,609
3-Chloropropionic acid,heptadecyl-ester	$C_{20}H_{39}ClO_2$	17.573	1,000,283–05–1	77.730	2,402	1,635
1-Dodecanol,3,7,11-trimethyl-	$C_{15}H_{32}O$	17.708	6,750–34–1	82.690	1,576	1,657
Tetradecane,2,6,10-trimethyl-	$C_{17}H_{36}$	17.821	14,905–56–7	79.830	1,671	1,668
7-Methyl-Z-tetradecen-1-ol acetate	$C_{17}H_{32}O_2$	17.895	1,000,130–99–6	78.550	2,171	1,671
Tetradecane,2,6,10-trimethyl-	$C_{17}H_{36}$	18.100	14,905–56–7	86.680	1,671	1,678
Dichloroacetic acid,heptadecyl	$C_{19}H_{36}Cl_2O_2$	18.165	1,000,282–98–2	83.040	2,423	1,683
1-Hexadecanesulfonyl chloride	$C_{13}H_{33}ClO_2S$	18.270	38,775–38–1	81.020	2,295	1,691
1-Heptadecene	$C_{17}H_{34}$	18.436	6,765–39–5	88.600	1,687	1,703
1-Hexadecanol,2-methyl-	$C_{17}H_{36}O$	18.545	2,490–48–4	80.430	1,761	1,735
1-Decanol, 2-hexyl-	$C_{16}H_{34}O$	18.724	2,425–77–6	87.980	1,774	1,760
1-Hexade canesulfonyl chloride	$C_{16}H_{33}ClO_2S$	19.338	38,775–38–1	82.920	2,295	1,943
1-Hexade canesulfonyl chloride	$C_{16}H_{33}ClO_2S$	19.644	38,775–38–1	77.210	2,295	1,981
PP:PS: PVC						
Benzene	C_6H_6	4.523	71–43–2	75.830	647	621
Ethane,1,1-diethoxy-	$C_6H_{14}O_2$	6.904	105–57–7	92.340	718	702
Ethane,1,1-diethoxy-	$C_6H_{14}O_2$	7.144	105–57–7	84.620	718	714
Toluene	C_7H_8	7.828	108–88–3	75.060	757	755
1-Heptene, 2-methyl-	C_8H_{16}	8.556	15,870–10–7	76.400	696	797

(*Cont'd...*)

Table S1. *Continued*

Compound	Chemical formula	RT	CAS	Score	RI_{lib}	RI_{exp}
2,4-Dimethyl-1-heptene	C_9H_{18}	10.108	19549–87–2	95.730	897	902
Ethylbenzene	C_8H_{10}	10.688	100–41–4	83.88	790	915
Styrene	C_8H_8	11.447	100–42–5	96.770	828	932
2-Heptanone,4-methyl-	$C_8H_{16}O$	12.581	6,137–06–0	73.360	934	958
Decane,2-methyl-	$C_{11}H_{24}$	14.189	6,975–98–0	86.200	936	995
Nonanoyl chloride	$C_9H_{17}ClO$	14.421	764–85–2	73.350	1,216	1,002
Cyclopropane,1-butyl-1-methyl-2-propyl-	$C_{11}H_{22}$	14.599	41,977–34–8	77.450	1,059	1,017
Cyclopentane,1-butyl-2-propyl-	$C_{12}H_{24}$	15.231	62,199–50–2	85.040	1,085	1,069
1-Octanol,2,7-dimethyl-	$C_{10}H_{22}O$	15.301	15,250–22–3	84.700	1,043	1,075
Dodecane,4,6-dimethyl-	$C_{14}H_{30}$	15.602	61,141–72–8	80.690	1,226	1,205
Cyclopentane,1,2-dibutyl-	$C_{13}H_{26}$	16.038	62,199–52–4	80.750	1,289	1,319
Tetradecane,2,6,10-trimethyl-	$C_{17}H_{36}$	18.100	14,905–56–7	75.280	1,677	1,710
1-Hexadecanol,2-methyl-	$C_{17}H_{36}O$	18.436	2,490–48–4	80.830	1,761	1,744
1-Decanol,2-hexyl-	$C_{16}H_{34}O$	18.719	2,425–77–6	86.520	1,774	1,772
1-Decanol,2-hexyl-	$C_{16}H_{34}O$	18.959	2,425–77–6	86.120	1,774	1,796
11,13-Dimethyl-12-tetradecen-1-ol acetate	$C_{18}H_{34}O_2$	19.705	1,000,130–81–0	72.580	1,968	1,971

Notes: RT, retention time; RI_{exp}, a series of alkanes (C_2–C_{20}) was used to calculate the retention index, $RI = 100\,n + 100 \times (t_x - t_n)/(t_{n+1} - t_n)$; t_x: Retention time of compound, t_n and t_{n+1}: Retention times of n-alkanes with carbon atom number n and n + 1; RI_{lib}, the retention index in the NIST library. Abbreviations: CAS: Chemical Abstracts Service; PP: Polypropylene; PS: Polystyrene; PVC: Polyvinyl chloride.

Table S2. Two-dimensional correlation spectroscopy results on the assignment and sign of each cross-peak in synchronous and asynchronous maps of volatile organic compounds from plastic combustion

Polymer	Peak (cm^{-1})	Band assignments	Sign[a]				
			1,300–1,100 cm^{-1}	1,450–1,300 cm^{-1}	1,600–1,500 cm^{-1}	1,750–1,700 cm^{-1}	1,800–1,750 cm^{-1}
PP	1,300–1,100cm^{-1}	alcohols ethers	+	+(+)	+(+)	+(+)	+(+)
	1,450–1,300cm^{-1}	aliphatic hydrocarbons		+	+ (−)	+ (−)	+ (−)
	1,600–1,500cm^{-1}	aromatics			+	+(+)	+(+)
	1,750–1,700cm^{-1}	aldehydes ketones esters				+	+(−)
	1,800–1,750cm^{-1}	acids					+
PS	900–650cm^{-1}	Aromatics	+	+(+)	+(+)	+(−)	
	1,450–1,300cm^{-1}	aliphatic hydrocarbons		+	+(−)	+(−)	
	1,750–1,700cm^{-1}	aldehydes ketones esters			+	+(−)	
	1,800–1,750cm^{-1}	acids				+	
PVC	730–570cm^{-1}	chlorinated hydrocarbons	+	+(+)	+(+)	+(+)	+(+)
	1,450–1,300cm^{-1}	aliphatic hydrocarbons		+	+(−)	+(−)	+(−)
	1,600–1,500cm^{-1}	aromatics			+	+(+)	+(−)
	1,750–1,700cm^{-1}	aldehydes ketones esters				+	+(−)
	1,800–1,750cm^{-1}	acids					+
PP:PS: PVC	730–570cm^{-1}	chlorinated hydrocarbons	+	+(−)	+(−)	+(−)	+(−)
	1,450–1,300cm^{-1}	aliphatic hydrocarbons		+	+(−)	+(−)	+(−)
	1,600–1,500cm^{-1}	aromatics			+	+(+)	+(−)
	1,750–1,700cm^{-1}	aldehydes ketones esters				+	+(−)
	1,800–1,750cm^{-1}	acids					+

Note: (i) PP plastic combustion VOCs in sequence according to temperature: alcohols/ethers>aromatics>aldehydes/ketones/esters>aliphatic hydrocarbons>acids; (ii) PS plastic combustion VOCs in sequence according to temperature: acids>aromatics> aldehydes/ketones/esters>aliphatic hydrocarbons , (iii) PVC plastic combustion VOCs in sequence according to temperature: chlorinated hydrocarbons>acids>aromatics>aldehydes/ketones/esters>aliphatic hydrocarbons, (iv) PP:PS:PVC plastic combustion VOCs in sequence according to temperature: acids>aromatics>aldehydes/ketones/esters>aliphatic hydrocarbons>chlorinated hydrocarbons. [a] indicates the cross-peak signal pair composed of the synchronous spectrum sign (outside the parentheses) and the asynchronous spectrum sign (inside the parentheses), which is used to analyze the dynamic relationships of different

volatile organic compounds during the combustion process. Here, the synchronous sign (+/-) indicates whether the variation directions of the signal intensities corresponding to the functional groups represented by the two wavenumber ranges are consistent, while the asynchronous sign, when combined with the synchronous sign and according to Noda's rules, further deduces the sequence in which the signals of these two substances occur. Abbreviations: PP: Polypropylene; PS: Polystyrene; PVC: Polyvinyl chloride; RFGs: Residual functional groups.

Table S3. Two-dimensional correlation spectroscopy results on the assignment and sign of each cross-peak in synchronous and asynchronous maps of residual solids from plastics combustion

Polymer	Peak (cm^{-1})	Band assignments	Sign[a]				
			900–600 cm^{-1}	1,300–1,000 cm^{-1}	1,750–1,700 cm^{-1}	3,100–2,800 cm^{-1}	3,200–3,600 cm^{-1}
PP	900–600 cm^{-1}	Aromatics C–H	+	+(−)	+(−)	+(−)	+(−)
	1,300–1,000 cm^{-1}	C–O		+	+(+)	+(−)	+(−)
	1,750–1,700 cm^{-1}	C=O			+	+(−)	+(−)
	3,100–2,800 cm^{-1}	C–H				+	+(−)
	3,200–3,600 cm^{-1}	O–H					+
PS	900–600 cm^{-1}	Aromatics C–H	+	+(+)	+(+)	+(+)	+(+)
	1,300–1,000 cm^{-1}	C–O		+	+(+)	+(−)	+(−)
	1,750–1,700 cm^{-1}	C=O			+	+(−)	+(−)
	3,100–2,800 cm^{-1}	C–H				+	+(−)
	3,200–3,600 cm^{-1}	O–H					+
PVC	730–570 cm^{-1}	C–Cl	+	+(+)	+(+)	+(+)	
	1,300–1,000 cm^{-1}	C–O		+	+(−)	+(+)	
	1,750–1,700 cm^{-1}	C=O			+	+(+)	
	3,100–2,800 cm^{-1}	C–H				+	
PP:PS:PVC	900–600cm^{-1}	Aromatics C–H	+	+(−)	+(+)	+(−)	+(+)
	1,300–1,000cm^{-1}	C–O		+	+(+)	+(−)	+(+)
	1,750–1,700cm^{-1}	C=O			+	+(−)	+(+)
	3,100–2,800cm^{-1}	C–H				+	+(+)
	3,200–3,600cm^{-1}	O–H					+

Notes: (i) PP plastic combustion RFGs in sequence according to temperature: O–H>C–H>C–O>C=O>aromatics C–H; (ii) PS plastic combustion RFGs in sequence according to temperature: aromatics C–H>O–H>C–H>C–O>C=O; (iii) PVC plastic combustion RFGs in sequence according to temperature: C–Cl>C=O>C–O>C–H; (iv) PP:PS:PVC plastic combustion RFGs in sequence according to temperature: C–H>C–O>aromatics C–H>C=O>O–H. a indicates the cross-peak signal pair consisting of the synchronous spectrum sign (outside the parentheses) and the asynchronous

spectrum sign (inside the parentheses). The synchronous sign (+/−) indicates whether the variation directions of the vibrational intensities of two functional groups are consistent under combustion-induced thermal perturbation.
Abbreviations: PP: Polypropylene; PS: Polystyrene; PVC: Polyvinyl chloride; RFGs: Residual functional groups.

Table S4. Hetero 2D-TG–FTIR/FTIR–COS characteristics and the relationships between the sequential temperature responses of VOCs and RFGs during plastics combustion

Polymer	Peak(cm^{-1})	Band assignments	Sign[a]						
			900–600 cm^{-1}	1,300–1,000cm^{-1}	1,450–1,300cm^{-1}	1,750–1,700cm^{-1}	1,800–1,750cm^{-1}	3,100–2,800cm^{-1}	3,600–3,200cm^{-1}
PP	900–600 cm^{-1}	Aromatics C–H	+	+(−)	+(−)	+(−)	+(−)	+(−)	+(−)
	1,300–1,000 cm^{-1}	Alcohols ethers		+	+(+)	+(+)	+(+)	+(+)	+(+)
	1,450–1,300 cm^{-1}	Aliphatic hydrocarbons			+	+(−)	+(+)	+(−)	+(−)
	1,750–1,700 cm^{-1}	Aldehydes Ketones Esters				+	+(+)	+(−)	+(−)
	1,800–1,750 cm^{-1}	Acids					+	+(−)	+(−)
	3,100–2,800 cm^{-1}	C–H						+	+(−)
	3,600–3,200 cm^{-1}	O–H							+
PS	900–600 cm^{-1}	Aromatics C–H	+	+(+)	+(+)	+(−)	+(+)	+(+)	
	1,450–1,300 cm^{-1}	Aliphatic hydrocarbons		+	+(−)	+(−)	+(−)	+(−)	
	1,750–1,700 cm^{-1}	Aldehydes Ketones Esters			+	+(−)	+(−)	+(−)	
	1,800–1,750 cm^{-1}	acids				+	+(+)	+(+)	
	3,100–2,800 cm^{-1}	C–H					+	+(+)	
	3,600–3,200 cm^{-1}	O–H						+	

(*Cont'd...*)

Table S4. *Continued*

Polymer	Peak(cm^{-1})	Band assignments	Sign[a]						
			900–600 cm^{-1}	1,300–1,000cm^{-1}	1,450–1,300cm^{-1}	1,750–1,700cm^{-1}	1,800–1,750cm^{-1}	3,100–2,800cm^{-1}	3,600–3,200cm^{-1}
PVC	730–570 cm^{-1}	C–Cl	+	+(+)	+(+)	+(+)	+(+)	+(−)	+(+)
	900–650 cm^{-1}	Chlorinated hydrocarbons		+	+(+)	+(+)	+(+)	+(+)	+(+)
	1,450–1,300 cm^{-1}	Aliphatic hydrocarbons			+	+(−)	+(−)	+(−)	+(−)
	1,600–1,500 cm^{-1}	Aromatics				+	+(+)	+(−)	+(+)
	1,750–1,700 cm^{-1}	Aldehydes Ketones					+	+(−)	+(+)
	1,800–1,750 cm^{-1}	Esters						+	+(+)
	3,100–2,800 cm^{-1}	C–H							+
PP:PS:PVC	900–650 cm^{-1}	Chlorinated hydrocarbons	+	+(−)	+(−)	+(−)	+(−)	−(+)	+(−)
	1,450–1,300 cm^{-1}	Aliphatic hydrocarbons		+	+(−)	+(−)	+(−)	+(−)	+(−)
	1,600–1,500 cm^{-1}	Aromatics			+	+(+)	+(−)	+(−)	+(−)
	1,750–1,700 cm^{-1}	Aldehydes Ketones Esters				+	+(−)	+(−)	+(−)
	1,800–1,750 cm^{-1}	Acids					+	+(+)	+(+)
	3,100–2,800 cm^{-1}	C–H						+	+(+)
	3,600– 3,200 cm^{-1}	O–H							+

Notes: (i) The relationships between the sequential temperature responses of VOCs and RFGs of PP: ethers alcohols > O–H > C–H > aldehydes/ketones/esters > aliphatic hydrocarbons>acids>aromatics C–H; (ii) The relationships between the sequential temperature responses of VOCs and RFGs of PS:acids>aromatics C–H>O–H>C–H>aldehydes/ketones/esters>aliphatic hydrocarbons; (iii) The relationships between the sequential temperature responses of VOCs and RFGs of PVC:chlorinated hydrocarbons>acids> C–Cl > aromatics> aldehydes ketones esters >C–H >aliphatic hydrocarbons; (iv) The relationships between the sequential temperature responses of VOCs and RFGs of PP:PS: PVC: acids>C–H>O–H>aromatics>aldehydes/ketones/esters>aliphatic hydrocarbons>chlorinated hydrocarbons. [a] represents cross-peak signal pairs with synchronous and asynchronous symbols. They are used to track how functional groups or compounds change during plastic combustion as temperature rises. By analyzing these symbols, the order of changes in volatile compounds, solid residues, and free radicals can be determined, helping to clarify the stages and mechanisms of the combustion process.

Abbreviations: 2D-TG-FTIR/FTIR-COS: Two-dimensional thermogravimetric analysis–Fourier transform infrared spectroscopy/Fourier transform infrared correlation spectroscopy; PP: Polypropylene; PS: Polystyrene; PVC: Polyvinyl chloride; RFGs: Residual functional groups; VOCs: Volatile organic compounds.

Table S5. The E_α and R^2 values of the four plastics under different conversion rates

Plastic	Conversion rate (α)	FWO		KAS		STA	
		E_α (kJ/mol)	R^2	E_α (kJ/mol)	R^2	E_α (kJ/mol)	R^2
PP	0.1	68.807	0.999	78.276	0.999	69.497	0.999
	0.2	64.292	0.999	74.053	0.999	65.024	0.999
	0.3	63.261	0.994	73.246	0.996	64.030	0.994
	0.4	63.685	0.990	73.828	0.992	64.461	0.990
	0.5	65.099	0.984	75.383	0.988	65.886	0.984
	0.6	66.271	0.980	76.697	0.985	67.070	0.981
	0.7	68.166	0.981	78.700	0.986	68.959	0.982
	0.8	69.172	0.974	79.823	0.981	69.969	0.975
	0.9	70.977	0.969	81.752	0.977	71.784	0.970
	Avg.	66.637		76.862		67.409	
PS	0.1	115.515	0.966	115.556	0.972	116.066	0.966
	0.2	123.147	0.968	116.845	0.974	123.720	0.967
	0.3	129.391	0.963	132.675	0.969	139.318	0.964
	0.4	140.831	0.955	151.489	0.961	141.372	0.956
	0.5	156.536	0.947	167.319	0.954	157.036	0.984
	0.6	173.896	0.948	184.795	0.953	174.348	0.984
	0.7	182.509	0.952	193.517	0.963	182.938	0.952
	0.8	191.954	0.950	194.747	0.961	192.356	0.970
	0.9	192.910	0.951	195.795	0.973	193.325	0.992
	Avg.	156.299		161.415		157.831	
PVC-1	0.1	107.841	0.999	116.837	0.999	108.338	0.999
	0.2	114.791	0.999	124.053	0.999	115.288	0.999
	0.3	117.510	0.999	126.929	0.999	118.013	0.999
	0.4	118.292	0.999	127.836	0.999	118.816	0.999
	0.5	120.719	0.999	130.355	0.999	121.227	0.999
	0.6	124.560	0.999	134.288	0.999	125.062	0.999
	0.7	123.812	0.999	133.614	0.999	124.333	0.999
	0.8	125.375	0.999	135.294	0.999	125.899	0.999
	0.9	130.970	0.999	141.047	0.999	131.506	0.999
	Avg.	120.430		130.028		120.942	
PVC-2	0.1	278.793	0.979	291.472	0.980	288.070	0.979
	0.2	291.472	0.998	261.966	0.999	250.174	0.999
	0.3	273.86	0.998	244.632	0.998	232.663	0.998
	0.4	206.528	0.998	252.371	0.998	256.742	0.998
	0.5	254.308	0.999	258.931	0.999	260.569	0.999
	0.6	217.511	0.994	230.738	0.995	218.026	0.994
	0.7	228.494	0.993	208.656	0.998	228.985	0.996
	0.8	213.005	0.964	218.741	0.954	238.469	0.957
	0.9	249.586	0.969	251.648	0.953	255.525	0.950

(*Cont'd...*)

Table S5. *Continued*

Plastic	Conversion rate (α)	FWO		KAS		STA	
		E_α (kJ/mol)	R^2	E_α (kJ/mol)	R^2	E_α (kJ/mol)	R^2
PVC-2	Avg.	245.951		246.573		247.691	
PP-PS-PVC-1	0.1	84.104	0.968	93.299	0.974	84.706	0.968
	0.2	82.375	0.968	91.853	0.974	83.016	0.968
	0.3	77.977	0.973	87.655	0.979	82.378	0.974
	0.4	81.552	0.968	83.148	0.976	82.237	0.969
	0.5	71.093	0.985	81.211	0.989	71.817	0.985
	0.6	82.916	0.992	84.179	0.994	82.817	0.993
	0.7	83.564	0.983	84.055	0.986	84.316	0.984
	0.8	85.285	0.959	87.829	0.965	90.197	0.960
	0.9	88.843	0.959	91.579	0.956	89.609	0.955
	Avg.	881.968		87.201		83.455	
PP-PS-PVC-2	0.1	134.654	0.959	146.593	0.954	135.358	0.977
	0.2	137.206	0.975	149.344	0.954	146.019	0.976
	0.3	125.508	0.951	137.862	0.964	126.279	0.974
	0.4	109.961	0.982	122.515	0.963	122.544	0.983
	0.5	112.538	0.970	116.986	0.958	138.796	0.985
	0.6	139.243	0.954	135.709	0.978	140.030	0.957
	0.7	133.365	0.978	136.957	0.961	132.144	0.964
	0.8	131.685	0.988	140.872	0.982	139.202	0.969
	0.9	133.473	0.979	144.107	0.985	140.991	0.965
	Avg.	128.626		136.772		135.707	

Abbreviations: Avg: Average; E_α: Activation energy; FWO: Flynn–Wall–Ozawa; KAS: Kissinger–Akahira–Sunose; PP: Polypropylene; PS: Polystyrene; PVC: Polyvinyl chloride; R^2: Coefficient of determination; RFGs: Residual functional groups; STA: Starink.

References

1. Noda I, Allen WM, Lindberg SE. Two-dimensional Raman correlation spectroscopy study of an emulsion copolymerization reaction process. *Appl Spectrosc.* 2009;63(2):224-232.

   doi: 10.1366/000370209787392012

2. Song F, Wu F, Xing B, *et al.* Protonation-dependent heterogeneity in fluorescent binding sites in sub-fractions of fulvic acid using principal component analysis and two-dimensional correlation spectroscopy. *Sci Total Environ*. 2018;616:1279-1287.

   doi: 10.1016/j.scitotenv.2017.10.190

3. Noda I. Two-dimensional infrared (2D IR) spectroscopy: theory and applications. *Appl Spectrosc.* 1990;44(4):550-561.

   doi: 10.1366/0003702904087398

4. Chen W, Qian C, Liu X Y, *et al.* Two-dimensional correlation spectroscopic analysis on the interaction between humic acids and TiO_2 nanoparticles. *Environ Sci Technol.* 2014;48(19):11119-11126.

   doi: 10.1021/es502502n

5. Noda I. Close-up view on the inner workings of two-dimensional correlation spectroscopy. *Vib Spectrosc.* 2012;60:146-153.

   doi: 10.1016/j.vibspec.2012.01.006

6. Zhou Q, Sun S, Zhan D, *et al.* Point-point and point-line moving-window correlation spectroscopy and its applications. *J Mol Struct*. 2008;883:109-115.

   doi: 10.1016/j.molstruc.2008.01.019