

Particle Production by Polymer Pyrolysis: Effect of Carbon Monoxide

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Synopsis

The effects of carbon monoxide and water vapor on the production of condensation nuclei during the pyrolysis of various polymers were investigated. Carbon monoxide reduced nuclei production while H₂O increased it. The effect of the two combined was variable and unpredictable. The necessity for and the possible direction of additional investigation is pointed out.

INTRODUCTION

Van Luik and Ripperre reported the effect of various gases on the production of condensation nuclei from warm polymers.¹ Walther investigated this effect as a possible method of analyzing for trace gases in the atmosphere.^{2,3} Trace gas analyses are difficult because of low gas concentrations, interferences, and collection inefficiencies; a simple field method for the determination of carbon monoxide in the atmosphere would be desirable. Consequently, we have investigated the effect of CO on the production of condensation nuclei from a number of warm polymers of widely differing molecular architecture, with the view of developing a new analytical method.

EXPERIMENTAL

Equipment

The apparatus, shown in Figure 1, consisted of a gas source, a tube containing Ag₂O, a flowmeter, a bubbler to humidify the gas stream, a converter in which the gas stream reacted with the polymer, a nucleus counter and recorder, and the requisite valves, heater, stirrer, etc. The gas source is either room air passed through a Gelman Type E glass filter or filtered tank air having a dew point of -58°C and containing 105 ppm CO. The room air humidity varied from 20% to 40% (dew points from -2° to $+8^{\circ}\text{C}$), but it was usually near the midpoint of the range. Either gas flow could be diverted through a glass frit bubbler containing

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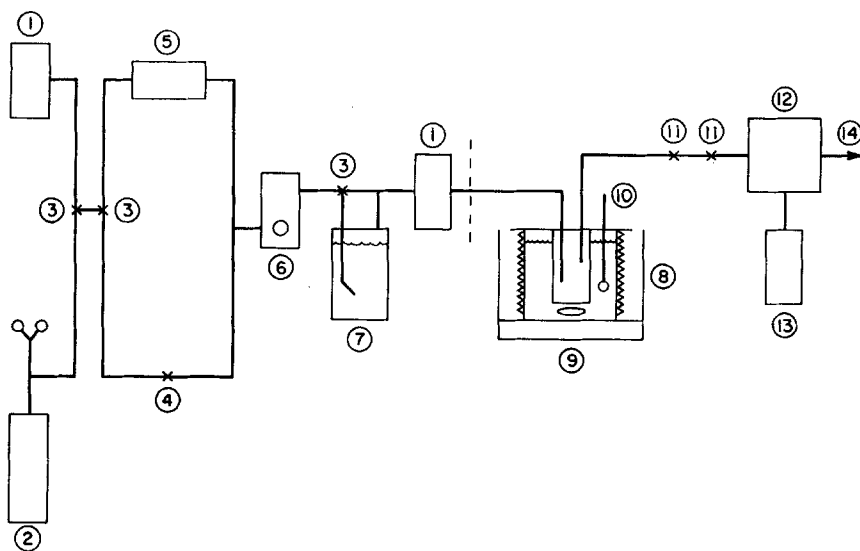


Fig. 1. Schematic of gas flow train: (1) Gelman Type E glass fiber filter; (2) cylinder of dry filtered air containing CO; (3) glass-Teflon three-way valve; (4) glass-Teflon needle valve; (5) tube containing Ag_2O ; (6) 10-LPM flowmeter; (7) glass frit humidifier; (8) stainless steel converter in insulated and air-lagged silicone oil bath; (9) temperature-controlled hot-plate magnetic stirrer; (10) thermometer; (11) glass-Teflon sampling valve; (12) GE continuous condensation nucleus counter with pump; (13) recorder; (14) to laboratory duct system. The flow train to the right of the vertical dashed line is stainless steel, except for two valves which consist of 15 cm glass and 4 cm Teflon.

ultrafiltered and deionized water, which we believe saturated the gas stream at 20°C . The converter was a 250-ml beaker fitted with a plug carrying inlet and outlet tubes, all of stainless steel. The plug was sealed into the beaker by a three-legged brass spider screwed to a brass clamping ring below the beaker flare. The temperature of the converter was held to within 0.2°C .

The General Electric continuous condensation nucleus counter was operated at approximately 23 cm (9 in.) Hg vacuum. A glass-Teflon needle valve in the line controlled the flow and maintained it at about 5.5 l./min as the various three-way valves were manipulated. The pressure drop across the tube containing Ag_2O was the greatest and therefore was the limiting factor on setting the flow level.

The upper operating temperature limit was set by the silicone oil bath, which began to smoke above 215°C . Smoke could interfere with accuracy of the nucleus count, despite the two glass fiber filters in the flow train.

A stainless steel beaker, washed, distilled-water rinsed, and air dried, is a copious source of nuclei when heated. Glass-shot blasting, followed by washing, rinsing, and drying, reduces the nucleus production at 200°C by over two orders of magnitude. Electropolishing in place of blasting reduces the output by another two orders of magnitude. Adding a 2-hr

bakeout at 300°C reduces the count by about one half. A low nucleus count can be obtained by washing, soaking in chromic acid glass-cleaning solution for 2 hr, distilled-water rinsing, and baking out. This last procedure was followed in this work. The nucleus count was typically 1000–2000 cm⁻³ at 200°C; it dropped to the filtered-air background of less than 100 cm⁻³ at 150°C. The room air typically contained 6000–8000 nuclei cm⁻³.

Polymers

The following polymers were investigated: ApC, Apiezon C (Biddle), a straight hydrocarbon oil; C-40, Chlorafin 40 (Hercules), a chlorinated wax; P-20 (Petrolite), a microcrystalline wax reacted with various (unspecified) resins; EVA (U.S. Industries), polyethylene/7% poly(vinyl acetate); PVA (U.S. Industries), poly(vinyl acetate); PS-2 (Dow), polystyrene; A-11, Acryloid A-11 (Rohm and Haas), poly(methyl methacrylate); PS2EHA (Environment/One), polystyrene/20% poly(2-ethylhexyl acrylate); SD, Porapak Q (Waters), polystyrene/50% poly(divinylbenzene); 914-De (Xerox), resin-coated glass beads; the resin may possibly consist of polystyrene, poly(methyl methacrylate), and poly(vinyl acetate); and SiG (Dow-Corning), silicone grease.

The purity of the P-20, PVA, PS2EHA, and 914-De are unknown. The SiG is a grease formulation containing a silica filler. The EVA contained an antioxidant. The remaining polymers were of commercial purity.

ApC and C-40 are liquids at room temperature. The flow temperatures of the polymers investigated, as determined with a Fisher-Johns melting point apparatus, are given in Table I.

If the clean stainless steel converter is loaded with a polymer and heated, the nucleus count remains at filtered-air background until some threshold

TABLE I
Polymer Characteristic Temperatures

Polymer	Flow temp., °C	Threshold temp., °C	Temperature at which $C^a =$	
			10 ⁴ cm ⁻³	10 ⁶ cm ⁻³
ApC	liquid	135	143	154
C-40	liquid	135	157	172
P-20	100	125	160	171
EVA	160	148	175	188
PVA	170	135	170	190
PS-2	115	130	166	192
A-11	215	165	175	200
PS2EHA	200	170	185	209
SD	>300	160	204	238
914-De	≈ 190 ^b	155	173	183
SiG	>300	150	163	181

^a C = concentration of condensation nuclei produced thermally in filtered room air.

^b Beads stuck together.

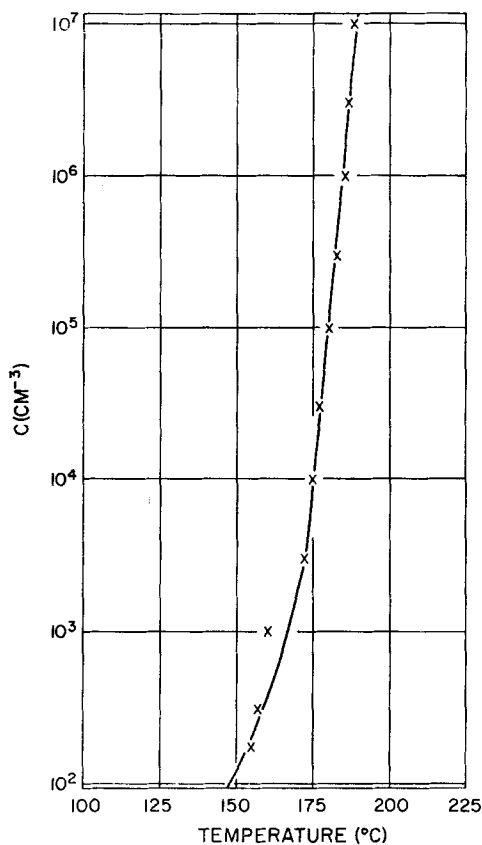


Fig. 2. Thermogram of EVA.

temperature is reached, whereupon it increases sharply with increasing temperature. A typical thermogram is shown in Figure 2. The threshold temperature tends to increase when the heating cycle is repeated, especially for the more refractory polymers; the increase is less marked for the softer polymers and very slight for those that are liquids. A nucleus count of 10^4 cm^{-3} is reached at widely varying temperatures above the threshold temperature, ranging from 8° to 44°C . These temperatures are only irregularly correlated with either flow or threshold temperatures, as Figures 3 and 4 show. The presence of liquids, solids, a crosslinked solid (SD), and a grease undoubtedly act to reduce the correlation. The repeatability of the temperature experiments varies, depending upon the relationship between the temperature at which 10^4 nuclei per cm^3 and the polymer's flow temperature are reached. If the former is above the flow temperature, repeatability is fair. However, if it is below the flow temperature, the temperature must be increased upon each cycle to reach this count.

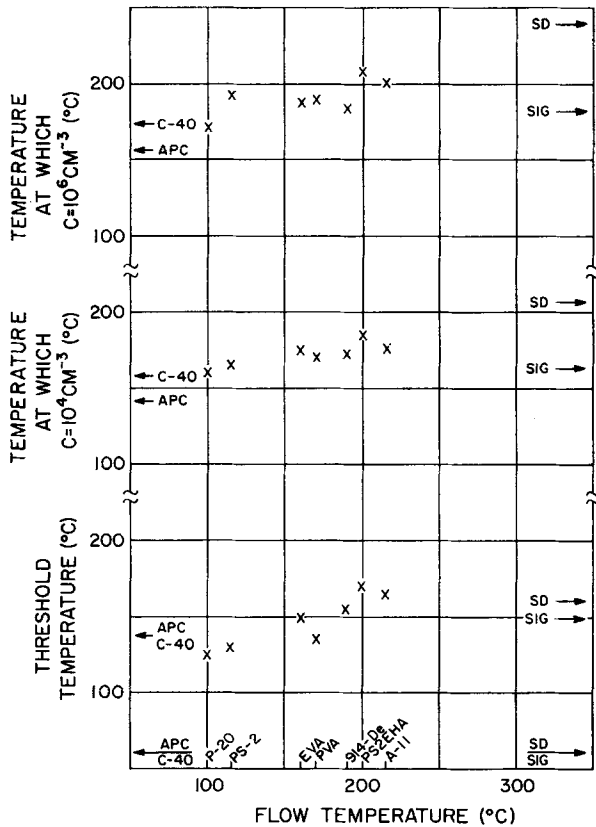


Fig. 3. Relationship between flow temperature and threshold temperature, temperature at which $C = 10^4 \text{ cm}^{-3}$, and temperature at which $C = 10^6 \text{ cm}^{-3}$. (Arrows indicate that flow temperatures were beyond the limits of this equipment.)

The same comments apply for the temperature at which 10^6 nuclei per cm^3 are reached.

Consequently, if one wishes to hold a given nucleus count level, the more refractory polymers require a slowly increasing temperature program. The softer polymers will hold a given level for extended periods at a fixed temperature. For instance, EVA gave a constant nucleus count at constant temperature for 14 hr distributed over two working days. P-20 performed similarly. For A-11 and those polymers listed after it (with the exception of 914-De), the temperature had to be increased approximately $2^\circ\text{C}/\text{hr}$ to keep the nucleus count approximately constant.

Method

The polymers, usually dissolved in a solvent, were placed in the converter beaker, and the solvent was evaporated to yield a film of polymer approximately $100\text{--}150 \mu\text{m}$ thick. Since no solvent was found for P-20,

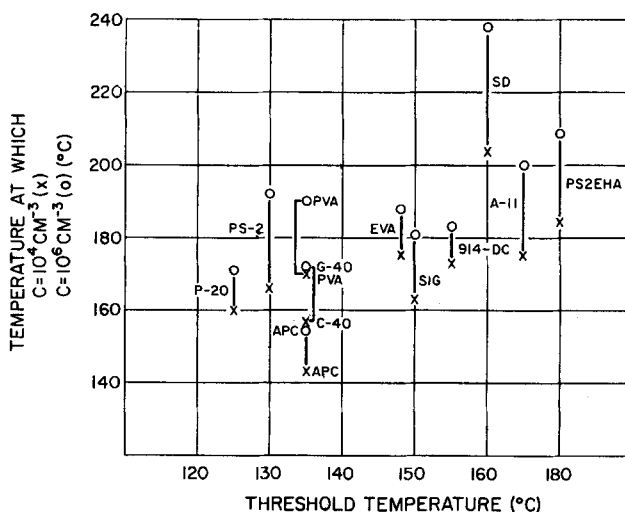


Fig. 4. Relationship between threshold temperature and the temperature at which $C = 10^4 \text{ cm}^{-3}$ (x) and $C = 10^6 \text{ cm}^{-3}$ (o).

it was weighed into the beaker and spread by melting. SD is highly crosslinked and hence insoluble, so it was merely weighed into the beaker. Since 914-De is approximately 80% glass beads, five times the usual weight was taken. Solvents for SiG caused the filler to clump, so it was applied directly to the beaker bottom by using a disk of polyurethane foam cemented to the end of a dowel. No allowance for filler was made when weighing.

The polymers in the converter were brought up to the working temperatures shown in Table II. The following sequence of nucleus counts was

TABLE II
Results of Experiments

Polymer	Solvent	C (Air) (10^8 nuclei/ cm^3)	E/C				Working temp., $^{\circ}\text{C}$
			H_2O	CO	CO+ H_2O	Ag_2O	
ApC	MEK	5-8	2.20	0.16	0.05	0.93	137
C-40	MEK	8	1.35	0.25	0.16	0.79	159
P-20	heat	3	2.33	0.77	0.57	0.87	156
PS-2	C_6H_6	1.3	1.96	0.32	2.85	0.61	177
EVA	warm CCl_4	3	3.33	0.50	2.00	2.67	160
PVA	C_6H_6	1.15	1.83	0.43	1.17	0.55	192
914-De	—	25	1.71	0.59	2.18	0.96	187
PS2EHA	C_6H_6	3.4-7	1.79	0.39	0.37	0.56	178-187.5
A-11	MEK	3-7.5	1.42	0.43	3.75	0.62	187-192
SiG	—	7	1.93	0.03	0.06	0.21	168-170
SD	—	1.3	1.77	0.50	0.51	0.92	203-206

then made (after stability had been attained at each operating condition; at least 10 min were allowed for this): (1) filtered room air; (2) humidified filtered room air; (3) filtered room air; (4) tank air containing 105 ppm CO; (5) filtered room air; (6) humidified tank air containing 105 ppm CO; (7) filtered room air; (8) room air diverted over Ag_2O ; and (9) filtered room air. Part or all of this sequence might be repeated.

RESULTS

The effect of the various experimental variables is expressed as an E/C ratio, where C is the concentration of condensation nuclei produced thermally in filtered room air and E is the concentration in the presence of the experimental variable. This is numerically identical to the signal-to-noise (S/N) ratio previously used^{2,3} but avoids imputing a new meaning to S/N , since S/N is a well known ratio in communications and electronics, where it is used to refer to the variations of a signal about its mean value, not to values in the presence and absence of a signal. See Table II for the results of the experiments.

Without exception, the addition of water vapor resulted in an enhancement of the E/C ratio. Also without exception, the addition of CO resulted in a reduction of the ratio.

The combined effect of water vapor and CO was variable, resulting with some polymers in an increase and with others in a decrease of the E/C ratio. The sense of the change was constant, but its magnitude was somewhat variable with any given polymer, as was true in the cases of water or CO alone. Changes in magnitude of 50% from one experimental cycle to another were not uncommon.

It is interesting that the E/C in the combined presence of CO and H_2O for 914-De is greater than unity, as are the E/C ratios for PVA, PS-2, and A-11, which are probably ingredients of 914-De. On the other hand, EVA, which contains 7% PVA, has an E/C of less than unity. PS2EHA, which contains 20% of a polyacrylate, also shows a decrease in nucleus output; A-11, which is 100% polyacrylate, shows an increase. Walther³ reported that PS2EHA in the presence of CO and H_2O carried in an 88% N_2 :12% O_2 stream exhibits an increase. SD, which is 50% polystyrene, also shows a decrease, although its highly crosslinked structure, which makes it somewhat different from the linear polymers, may explain this change. It is difficult to decide from such facts whether the operative variable is polymer composition or gas content.

Attempts to correlate graphically the E/C ratios observed in the joint presence of water vapor and CO with those observed in the individual presence of the two reactants were not notably successful. Even the correlation by rank was poor, but by magnitude it was very poor, whether the correlation was attempted by sum, difference, product, or quotient of the individual ratios or their logs.

Several runs were made with PS-2, admitting CO for times ranging

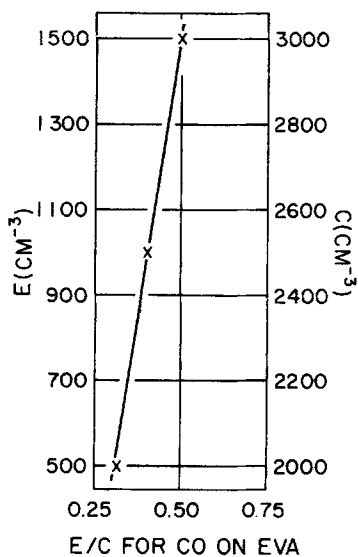


Fig. 5. Dependence of E/C on E and C for EVA with CO.

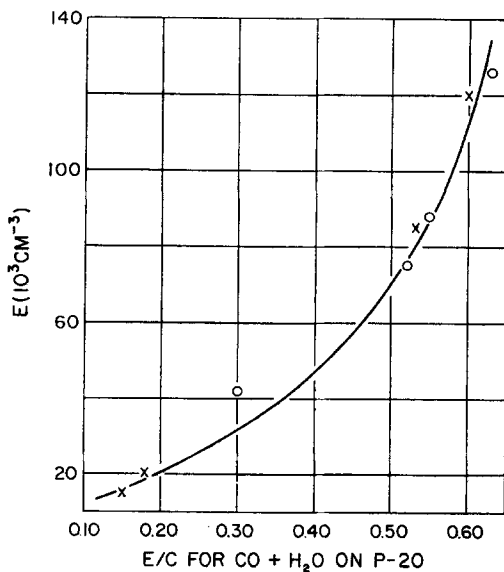


Fig. 6. Dependence of E/C on E for P-20 with CO and H₂O together.

from a fraction of a second to 1 min, in a search for transient effect. For additions of CO shorter than 5 sec, the transients observed on the 6 in./hr chart paper and on the nucleus counter meter looked like the valving transients obtained when the valves were operated without any change in the gas stream. For additions longer than 5 sec, there was a short-lived decrease in E . On the 1-min additions, the decrease was long enough and

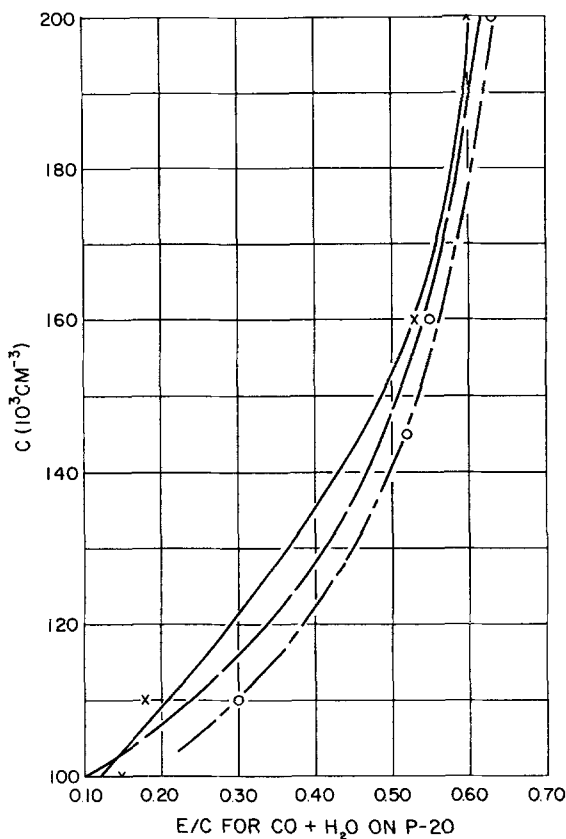


Fig. 7. Dependence of E/C on C for P-20 with CO and H₂O together.

pronounced enough to permit calculating E/C ratios. These were larger than those obtained in the usual 10–15 min runs, probably indicating that the 1-min addition had not allowed equilibrium to be attained.

Perhaps the most disquieting finding was that E/C not only depends on the content of the gas stream but is also a function of the nucleus count. Plots of the E/C ratios observed for CO on EVA and CO + H₂O on P-20, as shown in Figures 5–7, indicate a positive correlation with both E and C . Admittedly, there is a certain C value of the nucleus count due to thermal degradation of the polymer, and if the change to the E nucleus count depends on the gas stream concentration, then the E count includes both thermally produced nuclei and those due to the effect of the trace gas (the differences in the cases considered here), and E/C will increase as C increases. Alternatively, if the change due to the trace gas is a function of C , then E/C will again increase as C increases, depending upon how strong the function is. In either case, this phenomenon complicates using this technique as a method for determining CO in ambient air.

The results of passing the filtered room air over Ag₂O to remove CO

are also quite variable,⁴ even though the oxide was frequently changed. Since CO invariably caused E/C to be less than unity, we expected that the Ag_2O would slightly increase E/C . Three cases gave E/C only slightly below unity, and, in view of the variability experienced, we are probably safe in concluding that these three cases represent no change. In seven cases, E/C markedly decreased, and in the remaining case it nearly tripled. One would not expect the CO content of an air-conditioned building to be so variable. If the Ag_2O also removes some other active component of the gas stream, the same comment about variability applies, plus the possibility of there being one or more interferences to the determination of CO.

DISCUSSION

It is apparent that we do not have this method under sufficient control, nor do we yet know what all of the pertinent variables are. Theories of the mechanism of action were offered by Walther,³ but without supporting experimental data. Investigations with various gases and various polymers have increased the data but not our understanding. It would seem logical to select two polymers giving the largest changes in the opposite senses for study in a system incorporating a subsystem for adding water vapor and CO, both individually and simultaneously, each at two concentration levels, and to freeze out the converter output under every operating condition for subsequent mass-spectrometric analyses in order to ascertain what is happening in the converter. We do not currently know if this is a polymer problem, a surface problem, or a heterogeneous catalyst problem, although the last can probably be ruled out. Hopefully, the mass-spectrometric results would allow us to deduce the changes occurring in the converter so that we could begin to reason about the method.

The inconsistencies of data, the unpredictable changes in E/C produced by changes in operating variables, and the dependence of E/C upon E and C force the conclusions that a simple field method for determining CO is not at hand nor close to realization. Continued screening-type investigations are not apt to lead to progress. Only when the mechanism is understood can logic be applied to directing future investigations. Therefore, mass-spectrometric analyses should be done next.

One interesting speculation emerges from this work: that of the effect of air pollutants on polymeric items of commerce. Any polymer, heated in air, may experience enhanced reactivity with the low concentrations of trace impurities in the air. A few commercial products come immediately to mind: motor winding insulations, house paints, and roofing materials in sunlight and, probably most subject to attack, roadway paints on asphalt paving. These and kindred cases must be affected by air pollution. A second speculation relates to the possible effect upon human skin in sunlit polluted cities.

CONCLUSION

While it has been adequately demonstrated that CO does have an effect on the production of condensation nuclei from warm polymers, much more work must be done before a reliable method for measuring the CO in air by this technique is available.

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