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Polymer Degradation Initiated via Infectious Behavior

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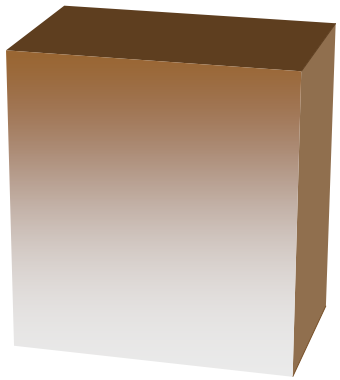
The challenge: Explore and understand interactive phenomena in polymer degradation

Examples of infectious processes

Ethylene gas ripens fruit

Unripe avocado + ripening apple



Ripening fruit releases ethylene, which causes OTHER fruit to ripen

$CH_2=CH_2$

ripe avocado

Tin disease causes infected metal to contaminate other metal

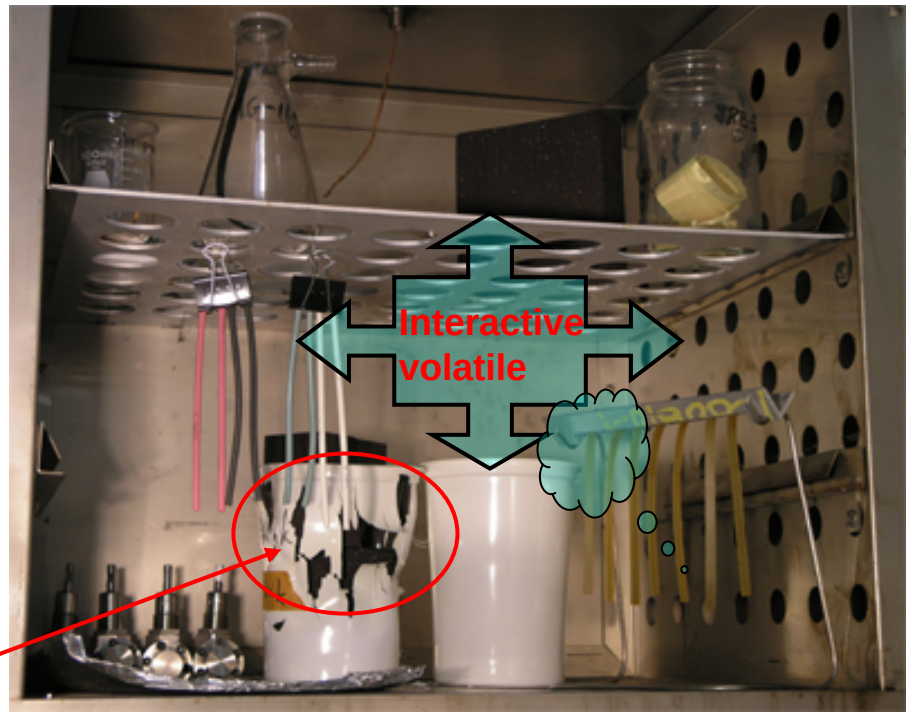
buttons degraded

Napoleon's army left Russia with their pants down

Accelerated aging of polymers

Could such phenomena exist in polymer degradation ?

- Various materials may age in single environment
- Suspected interaction effects were discussed in the 70's
- Gaseous degradation products may be important



Note: Perfomance of the container

Drake WO. *J. Polym. Sci. Polym. Symp. 57* (1977) 153
Sedlar J, Pac J. Polymer *15* (1974) 613

Infectious spreading of degradation disease

Prognosis isn't pretty

Many antique dolls wasting away as collectors face up to losses

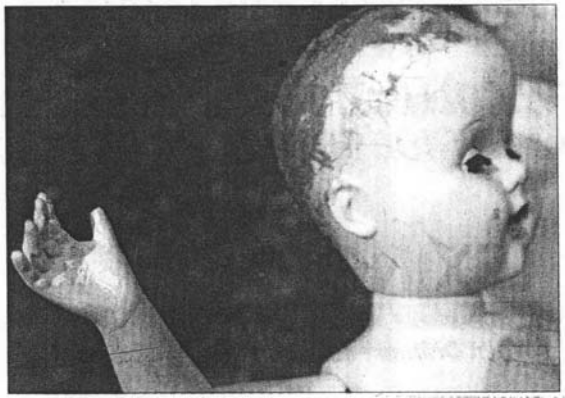
By Judith Gaines
GLOBE STAFF

HUDSON, N.H. – On a recent weekend, the huge hall of the Lions Club was full of dolls: rag dolls, ceramic dolls, dolls made from plastic and dolls made from wood, celebrity look-alike dolls representing the idols of generations of children.

But two dolls were under quarantine at the Hudson show, which featured the prized possessions of some of New England's best-known collectors. They had been banished from the hall – out of fear they would infect others.

"Keep them out of here," commanded Veronica Phillips, owner of the two ailing Saucy Walker dolls, when her husband brought them to her exhibit in

DOLLS, Page B4



A hard plastic doll shows signs of what some collectors call "sad doll disease."

Boston Globe 10/17/1996

Diseased dolls leave collectors at a loss

■ DOLLS
Continued from Page B1

the hall. Many of her antique dolls sell for hundreds of dollars, she said, but she would happily give those Saucy Walkers away.

If, as some say, dolls reflect the country's cultural history, then an entire era may be at risk. More and more of the hard plastic dolls of the 1940s and '50s are facing what collectors call "sad doll disease."

Although uncertain of the cause – oxidation, perhaps, or a chemical reaction caused by iron joints and eyes – collectors know the symptoms: Dolls reek with a foul, sour-milk smell, develop sticky patches on their bodies and, in extreme cases, cry viscous, vinegary tears.

Worse yet, the infection is contagious. "If you put them in a cabinet with other dolls, they'll contaminate them," said Phillips, a longtime collector in Dedham.

"For many of these dolls, the sense is that you can't do anything for them," said Dorothy McGonagle, who lives in Sudbury and is past president of Doll Collectors of America. "Most of us just toss them out. With that odor, they're too hard to live with. They smell like vomit. It's really gross."

Exactly how many dolls are afflicted is anybody's guess. Pat Aveni, who owns a doll hospital in Dover, N.H., estimates that 30 percent to 40 percent of the plastic dolls brought to her clinic have the sickness.

Sooner or later, says Nick Hill, a Scarborough, Maine, chemist, most of the plastic dolls from the 1940s and '50s will succumb. Hundreds of thousands of them were made.

Those were the early days of plastics production and, inevitably, the plastics deteriorate. Many fall victim to oxidation, he said, and heat can accelerate the process.

Howell Edwards, a chemist at the University of Bradford in England, diagnosed another aspect of the problem after an appeal from a British doll collector.

"She had her collection for 40 years and its value was emotional," Edwards said. "She'd had her dolls longer than she'd had her husband."

So Edwards and colleague Tony Johnson examined the woman's sick dolls with Raman spectroscopy, a process that uses laser beams to identify molecular compounds. They concluded that chemicals in the plastic reacted with iron bits in the dolls,

'Most of us just toss them out. With that odor, they're too hard to live with.'
DOROTHY McGONAGLE
Doll collector

producing a vinegary acid that slowly seeped from eye sockets and limb joints into other body parts, causing more degeneration.

"And vapors that escape from one infected doll can move into the body cavities of healthy neighboring dolls, which spreads the disease," Edwards said.

The plague is painful to doll lovers, not only because of the financial losses but also because they are losing a part of their own youths.

"A lot of people relate to that era because it was their childhood," said Jane Holtz, a doll dealer in Derry, N.H., who organized the show.

The at-risk dolls include some of the world's most popular models: Toni dolls with washable hair for girls who wanted to give them home permanents; Madame Alexander dolls with exquisitely detailed outfits; Little Ginnies, by Vogue; Saucy Walkers, by Ideal; American Character, Arranbee and Effanbee Co. dolls; Yes-No dolls that could shake their heads, and others that could blink or bat their eyes.

To combat doll disease, Edwards recommends washing the infected dolls in soapy water and drying them carefully to prevent further rusting. Hill is also developing some special sprays that are being tested.

But he said the remedies may merely slow the deterioration. And collectors at the Hudson show doubted that a cure could be found.

"The only answer is to sniff 'em before you buy 'em, and stay away from the stinky ones," said Sylvia Rose of Brunswick, Maine, a collector for more than 25 years.

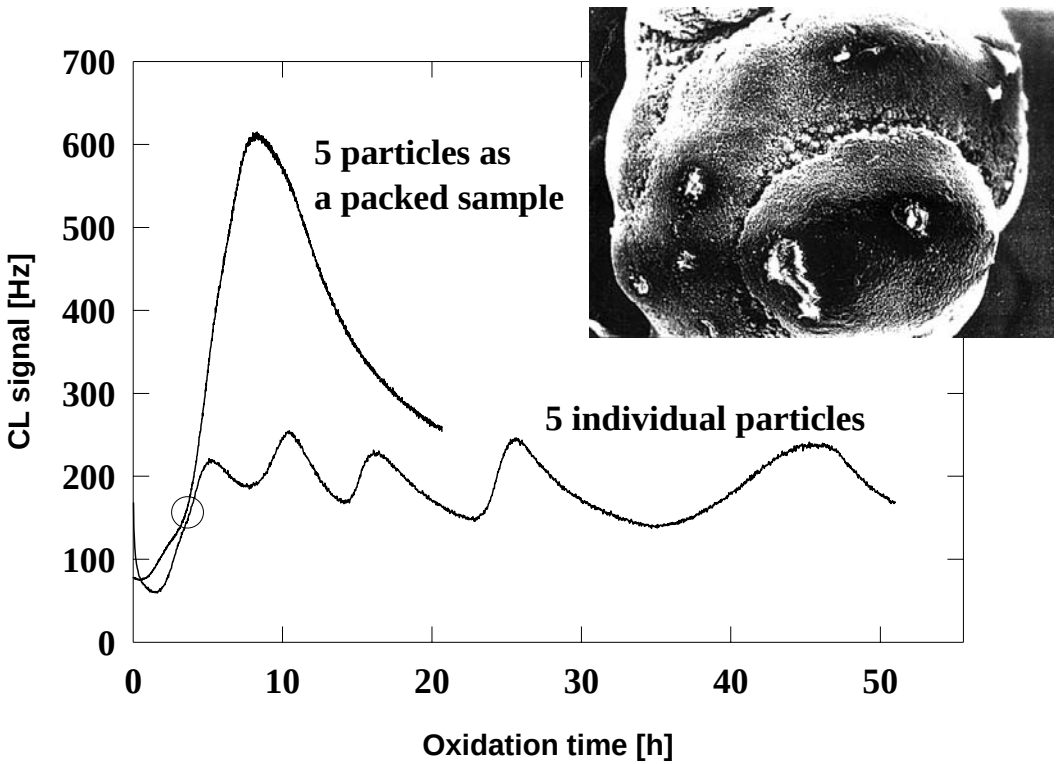
Advised Millie Caliri, a doll collector in South Lawrence, Mass.: "You just have to get used to the smell. It's kind of like having a dog – they always smell."

- **Antique doll exhibition**
- Wasting dolls as collectors face losses
- Quarantine, fear of infecting others
- Dolls from the 40 and 50's will succumb
- Inevitably plastics will deteriorate
- Vapours that escape can move to healthy specimens spreading the disease
- Doubtful a cure can be found
- Advice: sniff'em before you buy'em
- Or: Its kind of like having a dog, they always smell

- **The science involved**
- Polymers include polyvinylacetate,
- Hydrolytic degradation, autocatalysis
- Interior iron parts and oxidation products contribute
- Infectious intermediates !!

Prior evidence for infectious tendencies

- Weakest PP particle infects neighbors via gas phase
- Weakest particle controls the collective degradation of a sample
- Proposed model addressing heterogeneous nature of degradation
- Spreading of degradation through gas phase



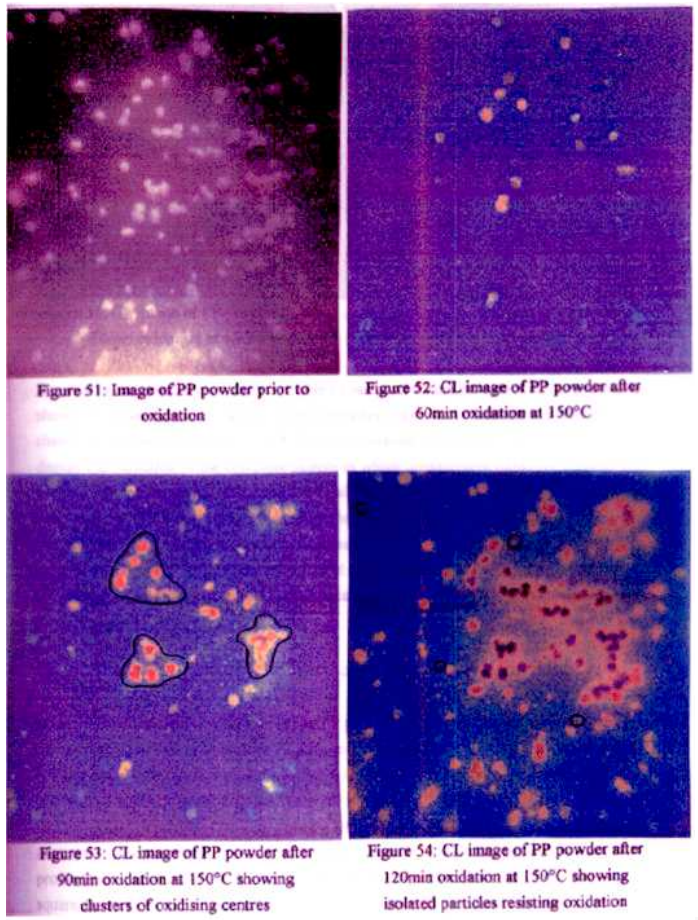


Figure 51: Image of PP powder prior to oxidation

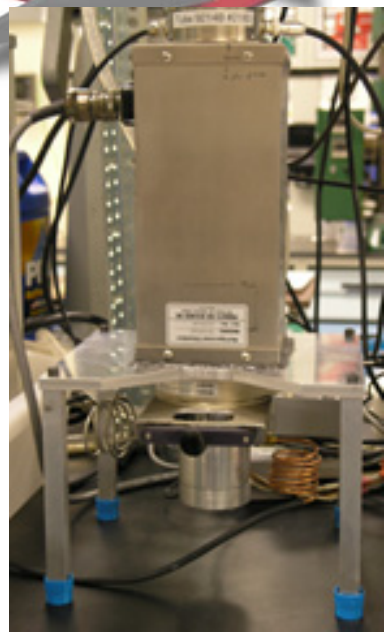
Figure 52: CL image of PP powder after 60min oxidation at 150°C

Figure 53: CL image of PP powder after 90min oxidation at 150°C showing clusters of oxidising centres

Figure 54: CL image of PP powder after 120min oxidation at 150°C showing isolated particles resisting oxidation

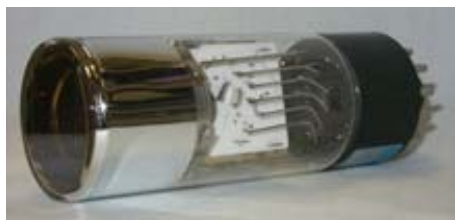
M. Celina, G. A. George, *Poly. Deg. Stab.*, *42* (1992) 335
M. Celina, G. A. George, *Poly. Deg. Stab.*, *40* (1993) 323
G. George, M. Celina, in *Handbook of Polymer Degradation II*, (2000) 277

CL in polymer degradation



- CL accompanies oxidative aging processes
- Weak photon emission in the visible
- Provides feedback on degradation processes
- Photon counting apparatus required
- Sensitive technique, mostly for fundamental studies
- In situ degradation studies, analysis of aged materials

sensitive photomultiplier detection



+ CL photon

aging
T, O_2

chemical condition probing

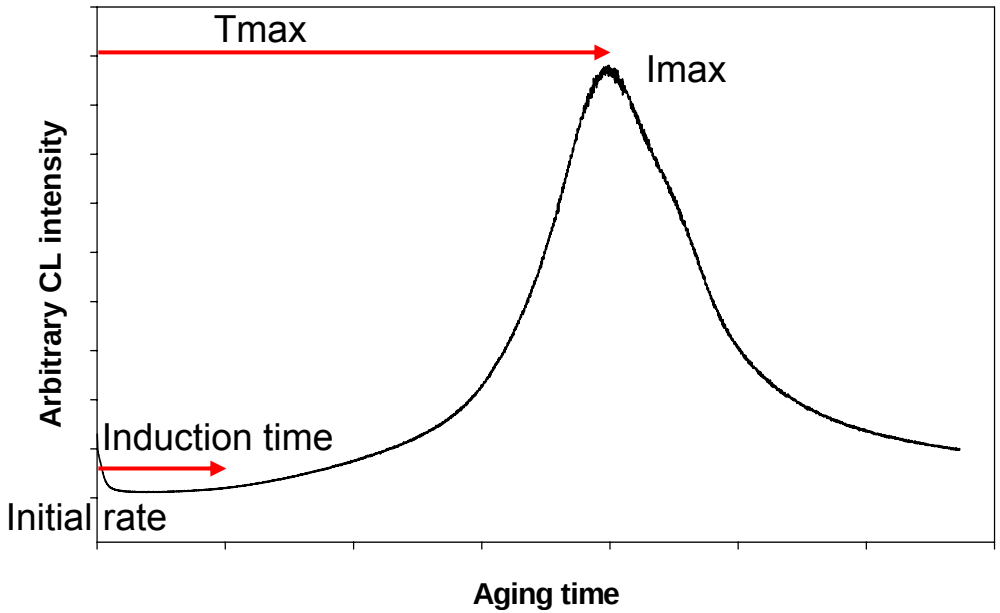
+ CL photon

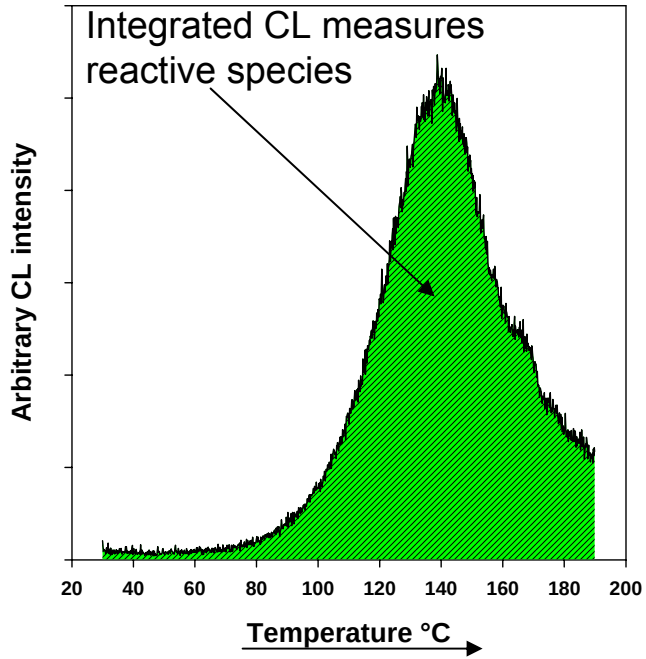
aged polymer,
chain defects with
reactive species, i.e. hydroperoxides

CL methods to investigate polymer degradation

- CL during isothermal aging
- Relative timing
- Monitors oxidation progress

- CL during inert T ramp
- Probe for reactive species





Objectives:

Study interaction of polymers, infectious activity
Probe for material interactions, organic/metallic
Develop methods to probe for subtle changes in polymers

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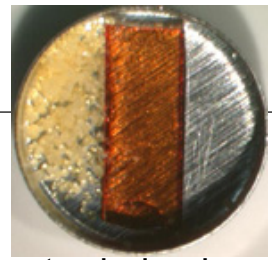
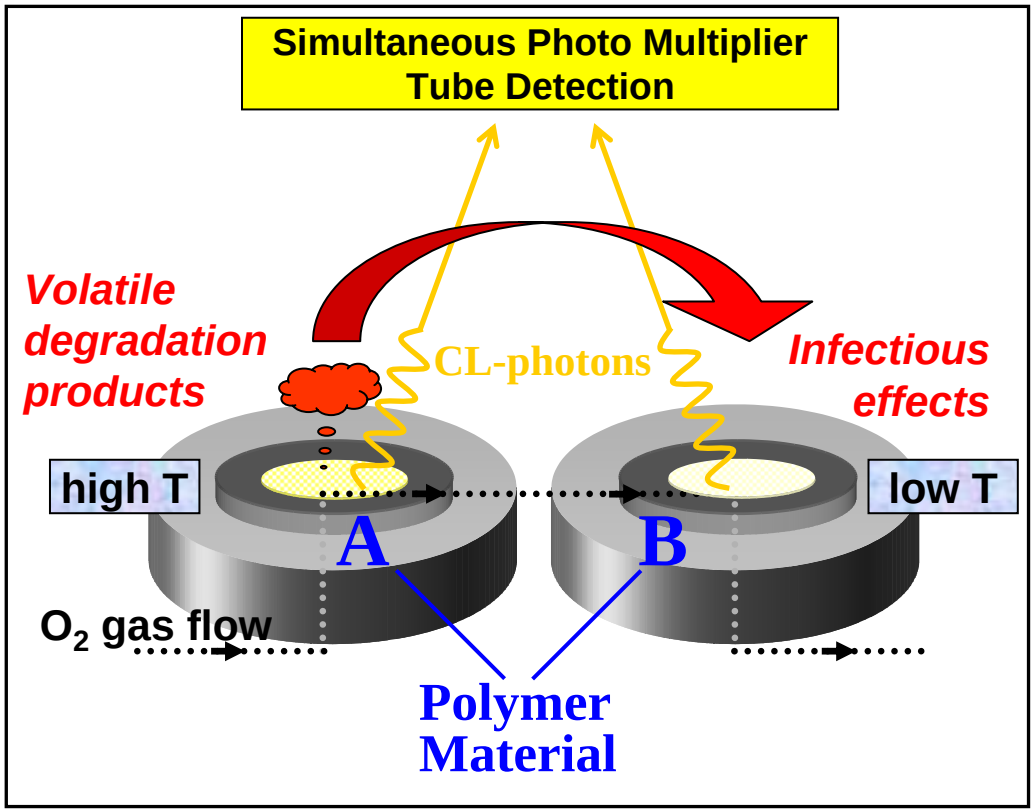
CL monitoring of interaction between materials

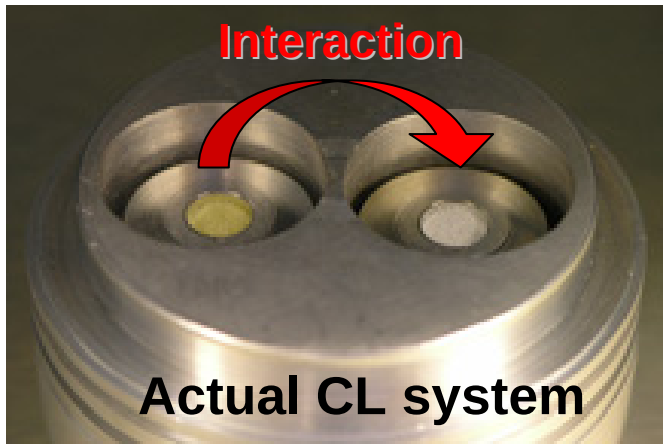
- CL provides feedback on material interaction
- Metal impurities often have detrimental impact on organics
- Organic materials can interact in complex fashion
- Observed faster and slower aging processes



CL provides fundamental insight into complex aging processes
How does such interaction depend on separation ?

New dual-stage CL system



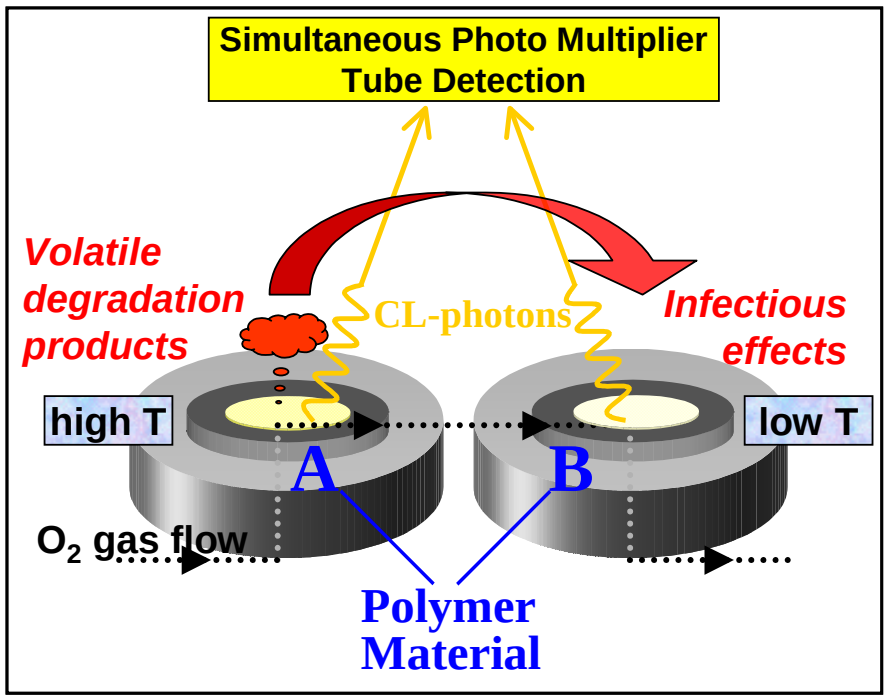


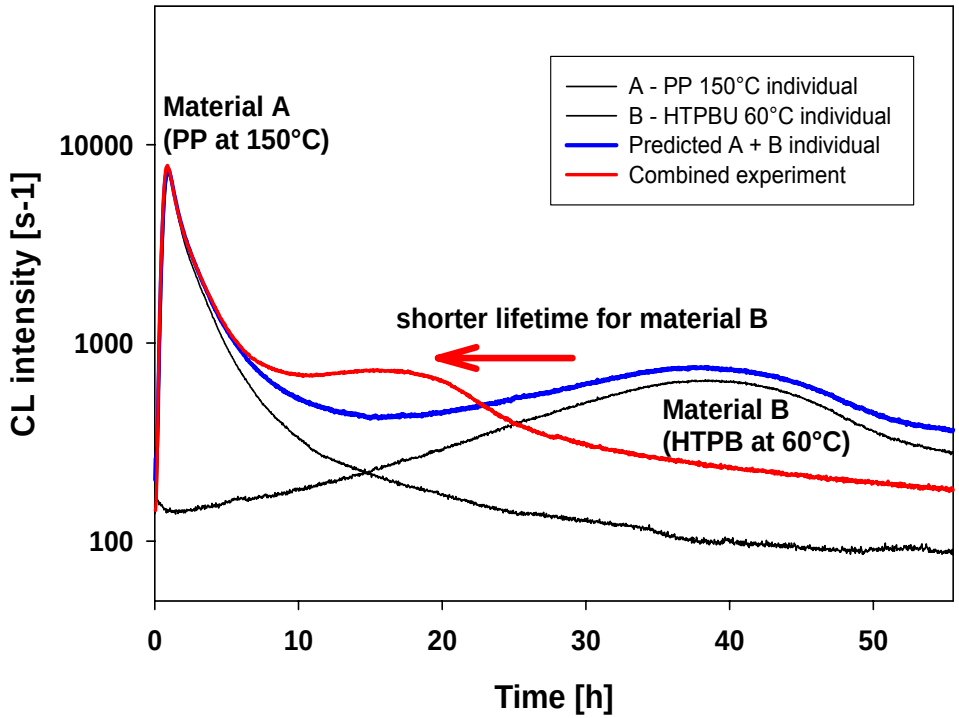
Innovative system:

Individual control of two hot-stages
Samples separated by ~ 25 mm
Joint large-diameter PMT detection
Adjustable carrier gas supply

CL monitoring of infectious polymer degradation

- Combined CL experiment for two polymers
- Can infectious agents initiate polymer degradation remotely ?



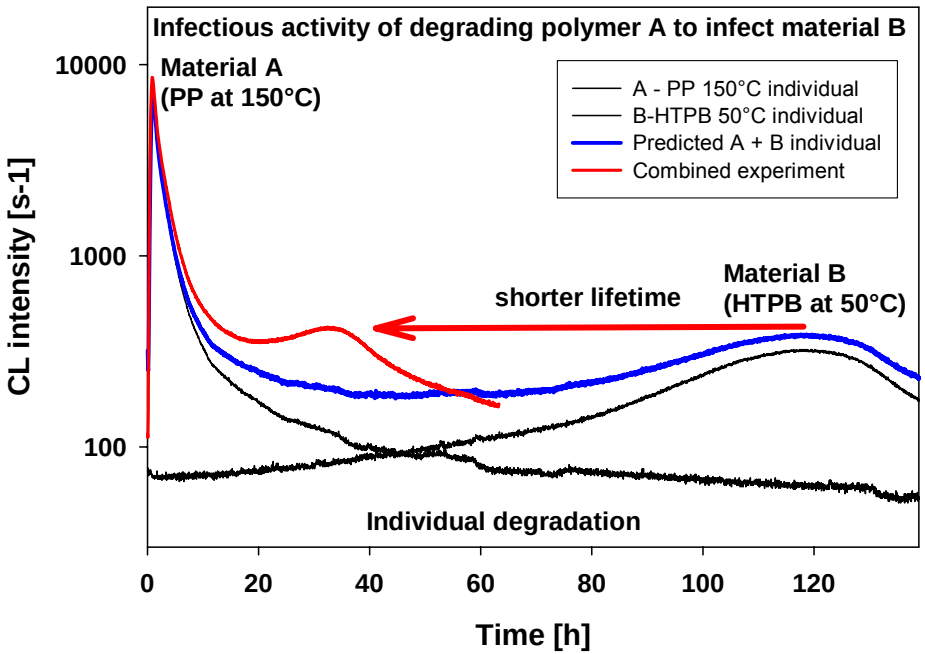


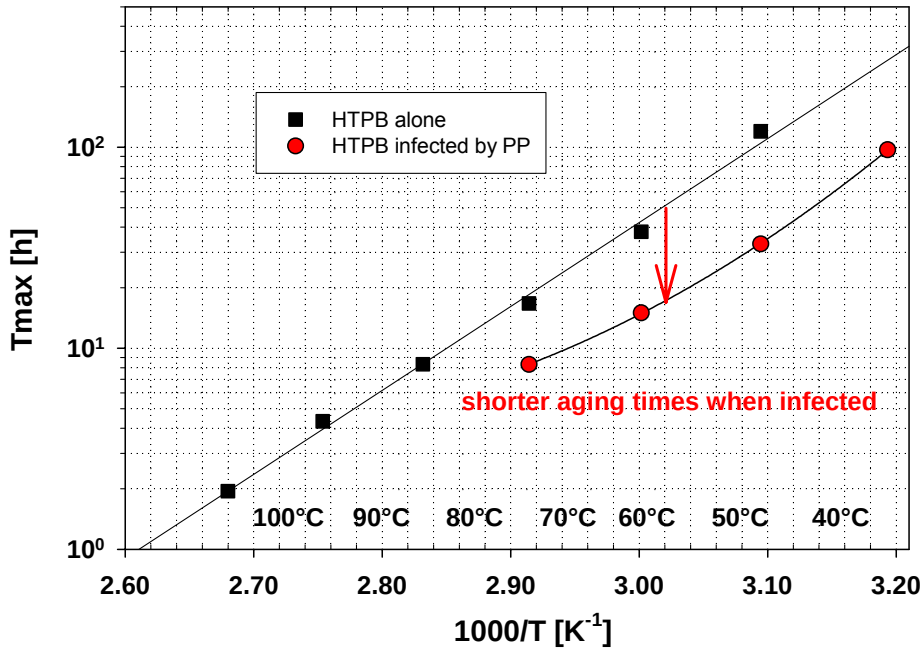
Experiments have shown for the first time that a degrading polymer can infect a different polymer

Must involve transfer of infectious species

Reactive agents initiate degradation

- CL used to monitor simultaneous degradation behavior
- Measures progress of oxidation in target sample
- Experiments showed that active PP infects HTPB
- Receiving material has faster degradation times at various T





Faster aging of HTPB when infected by degrading PP

What species might be involved ?

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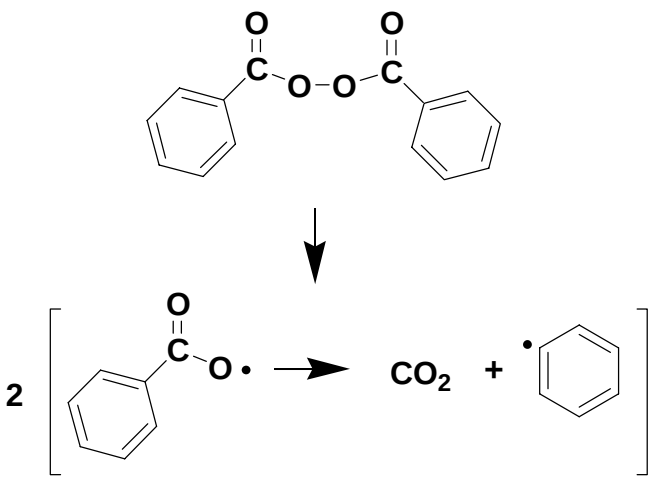
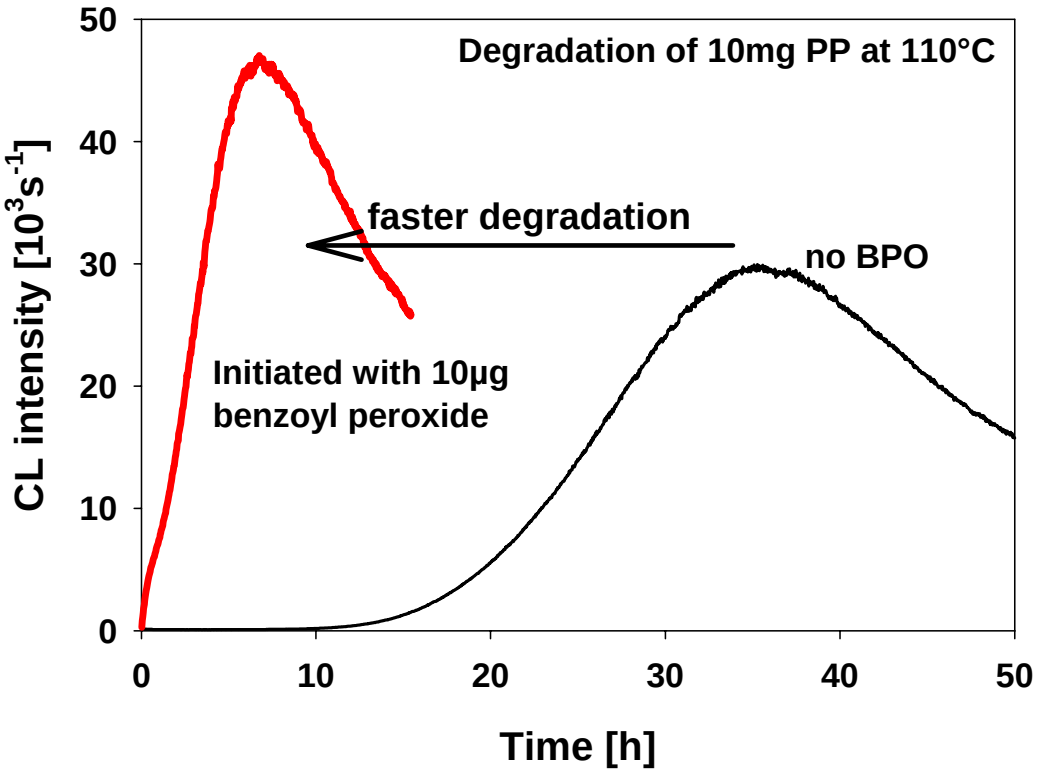
Degradation in the presence of peroxides

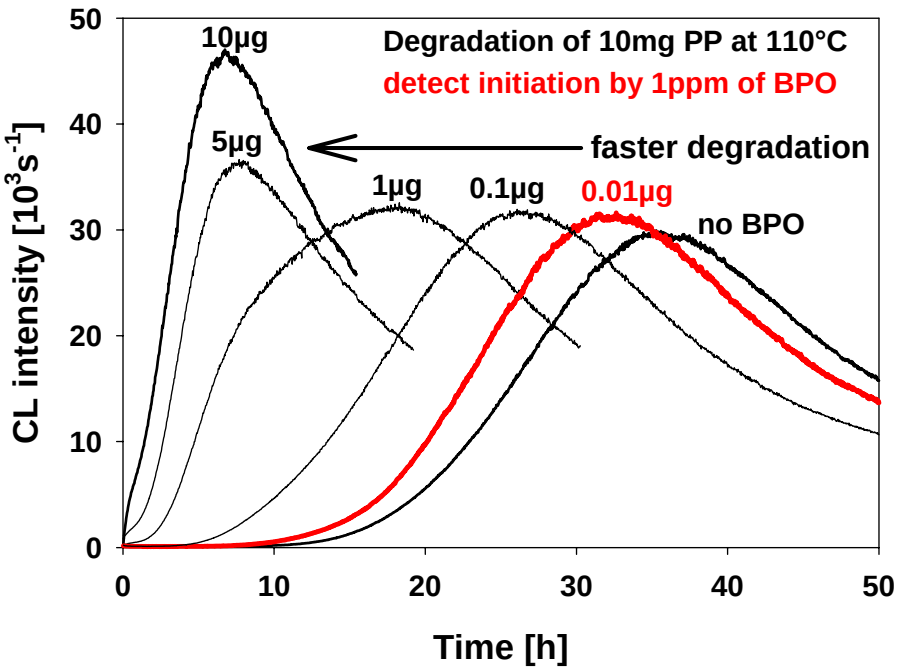
- Peroxides are thermally unstable and produce free radicals
- Peroxides will act as initiators for polymer degradation
- Will produce free radicals via thermal decomposition
- Small amounts have significant initiation potential

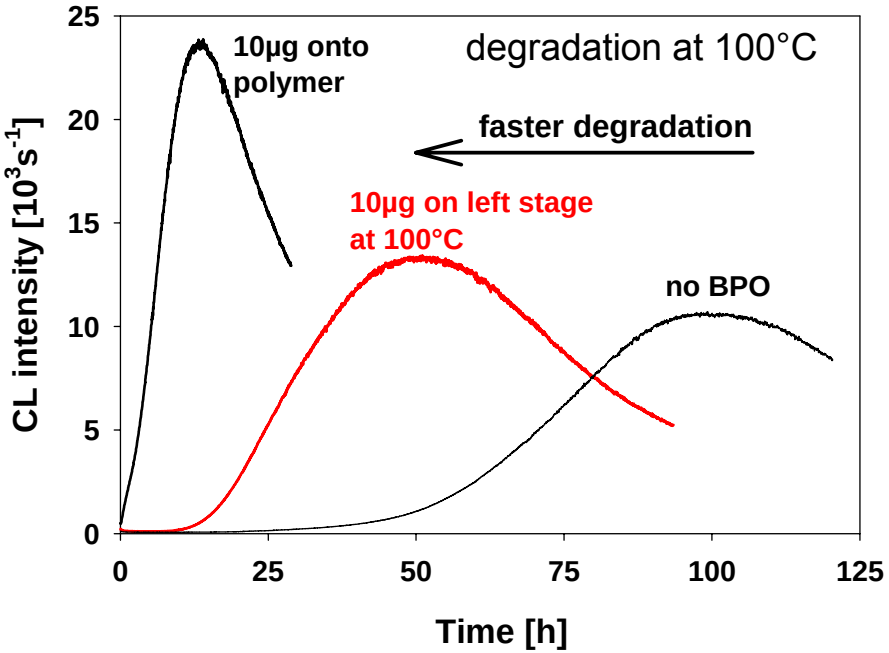




Benzoyl peroxide will initiate degradation

Reactive peroxides initiate degradation



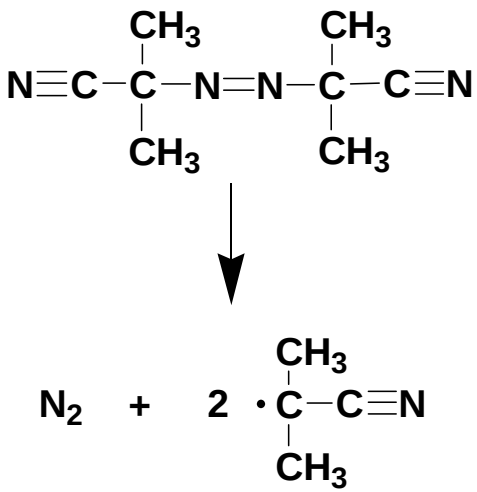


- **Peroxide (i.e. BPO) is an effective initiator for polymer degradation**
- **Even small amounts (ppm's) have initiation potential**
- **Most importantly: Remote initiation by peroxides is possible**

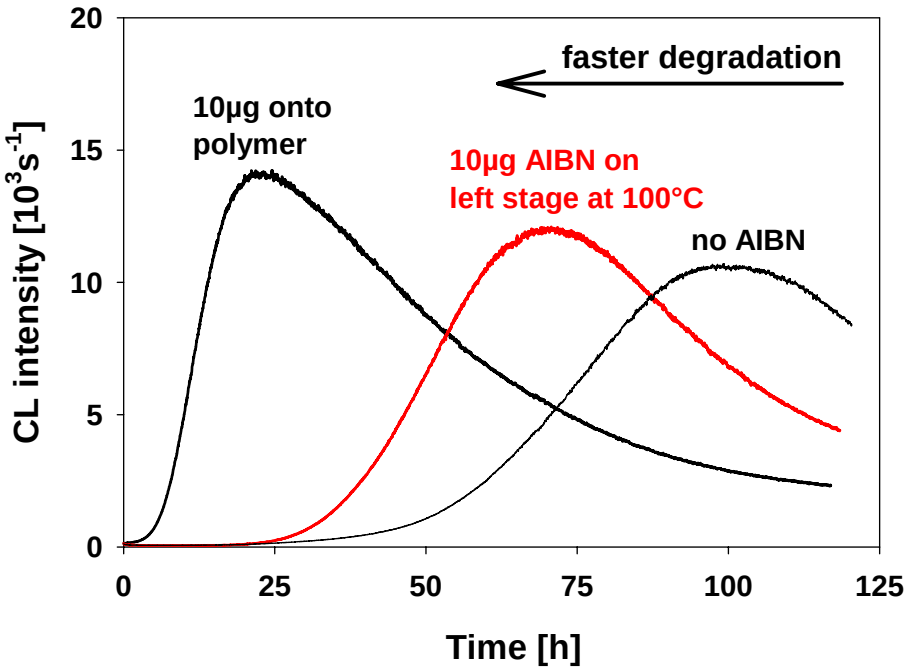
Proof of principle: Small quantities of benzoylperoxide can initiate degradation remotely

Remote initiation (example AIBN)

- AIBN has a suitable temperature sensitivity
- Mid-range molecular weight
- Similar to *tert.*-butyl peroxy radicals



10mg PP at 100°C inititated with AIBN at 100°C, i.e. 10µg (1000ppm)

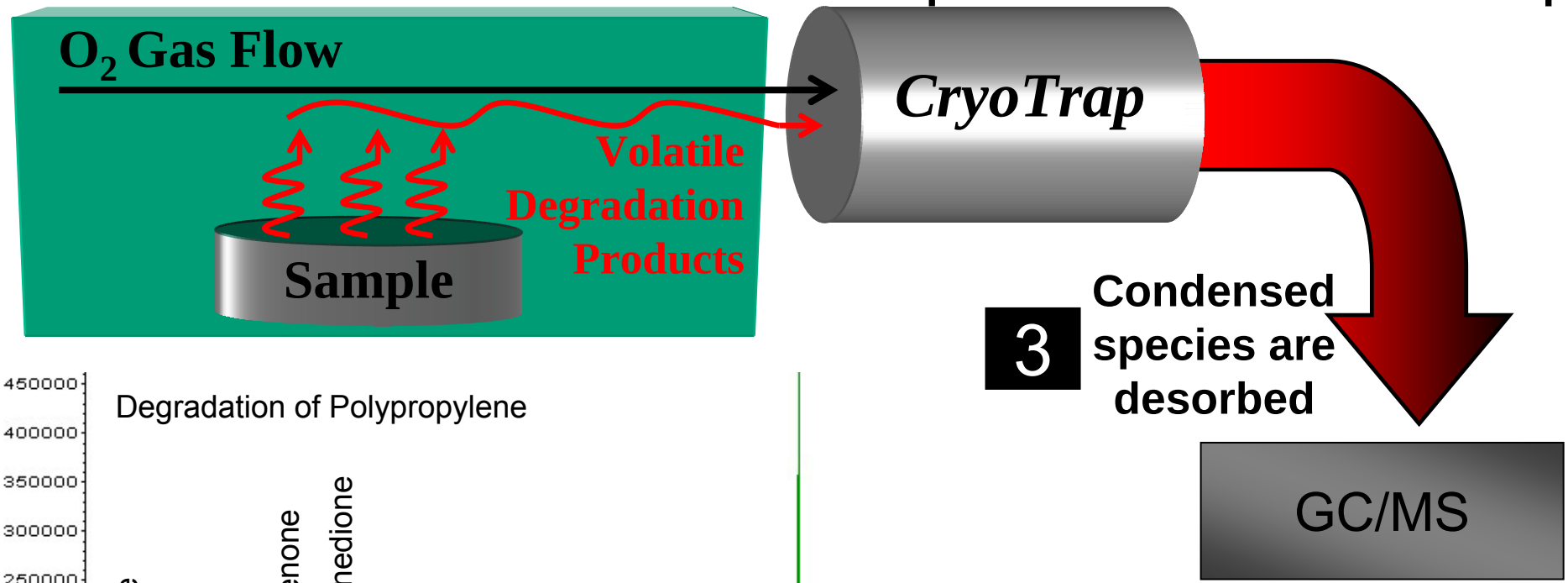


Different type of initiator can also act remotely

Target: Identification of volatiles

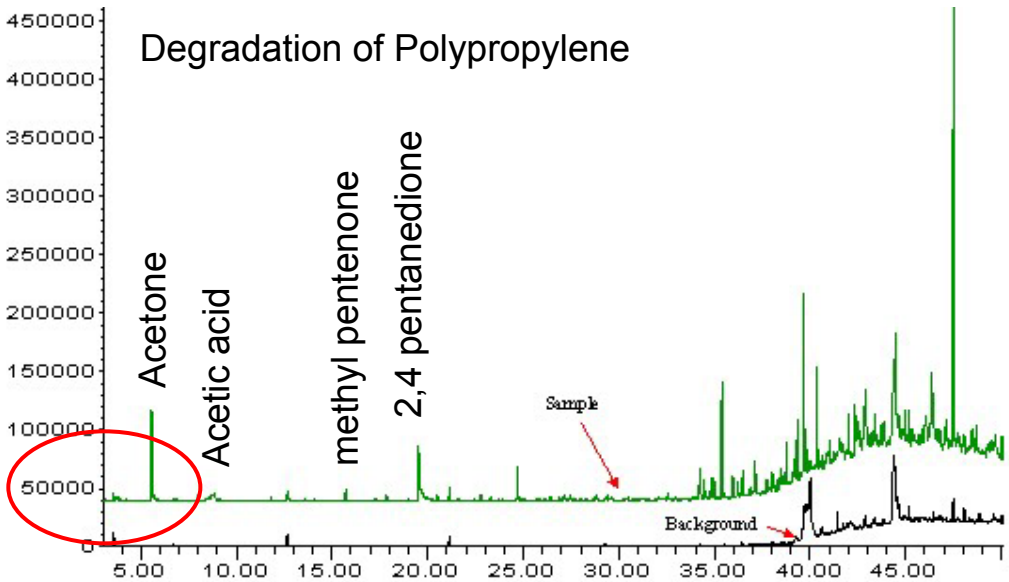
1 Sample is heated

2 Volatile trace intermediates are pre-concentrated via cold-trap



3 Condensed species are desorbed

GC/MS



4 Volatile components are analyzed by GC/MS

Target: Highly volatile peroxides, infectious intermediates during early degradation

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Explore low molecular weight peroxides

- **Synthesis of various peroxidic compounds (low M_w reagents)**
- **Tested these compounds for initiation tendencies**
- **Showed that dimethyl or diethyl peroxide, as well as peroxy-acetic acid does not act as an efficient initiator**
- **Initiation efficiency appears as a balance between volatility and adsorptive properties**
- **Thermal decomposition features complicate the situation further**

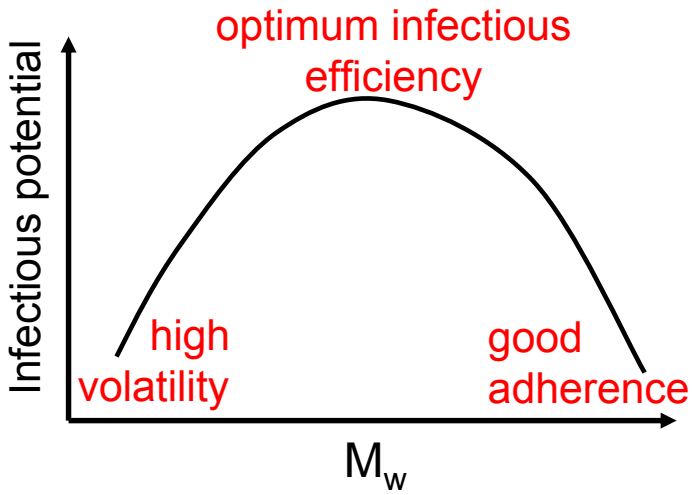
$R_1\text{-}R_2 + H_2O_2 \rightarrow R_1\text{-}OO\text{-}R_1 + HR_2$

$CH_3\text{-}OO\text{-}CH_3$ $CH_3CH_2\text{-}OO\text{-}CH_2CH_3$

$CH_3COOH + H_2O_2 \rightarrow CH_3\text{-}CO\text{-}OOH$

optimum molecular weight

$CH_3CH_2CH_2CH_2\text{-}OO\text{-}H$?



Remote inhibition processes ?

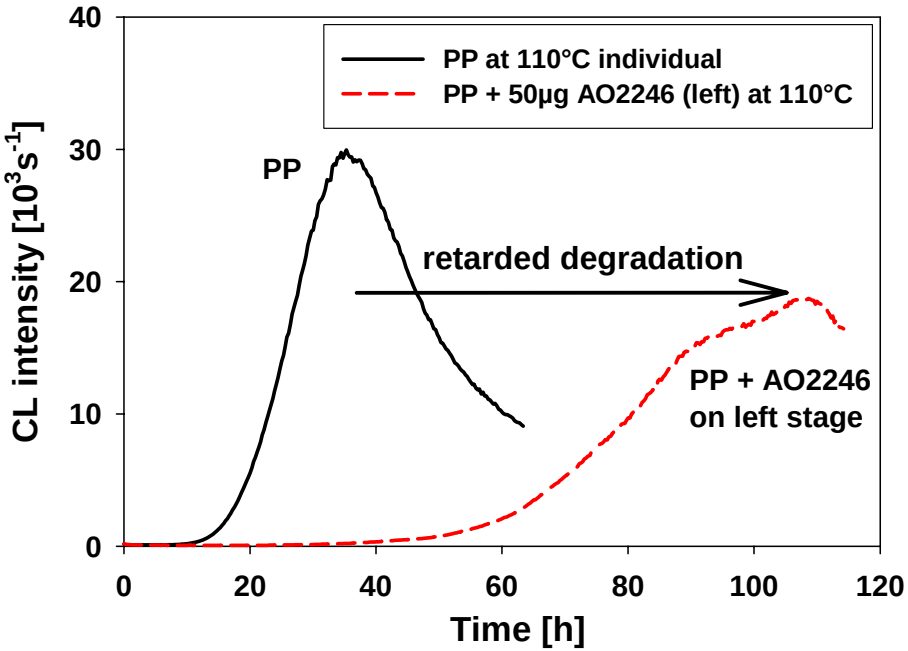
- Antioxidants are volatile substances, particularly at accelerated aging or processing conditions
- Suspected to be transferred in combined aging experiments
- Similarly, off-gasing of degradation products may be important in combined degradation experiments

Antioxidants have similar volatility and M_w as peroxidic species

Drake WO. *J. Polym. Sci. Polym. Symp. 57* (1977) 153
Sedlar J, Pac J. Polymer *15* (1974) 613

Transfer of inhibitious species (AO)

- Antioxidants are sufficiently volatile at elevated temperatures
- Spreading of AOs can lead to remote inhibition effects
- Proof of principle, fundamental studies



Evidence for transfer of antioxidant, remote inhibition

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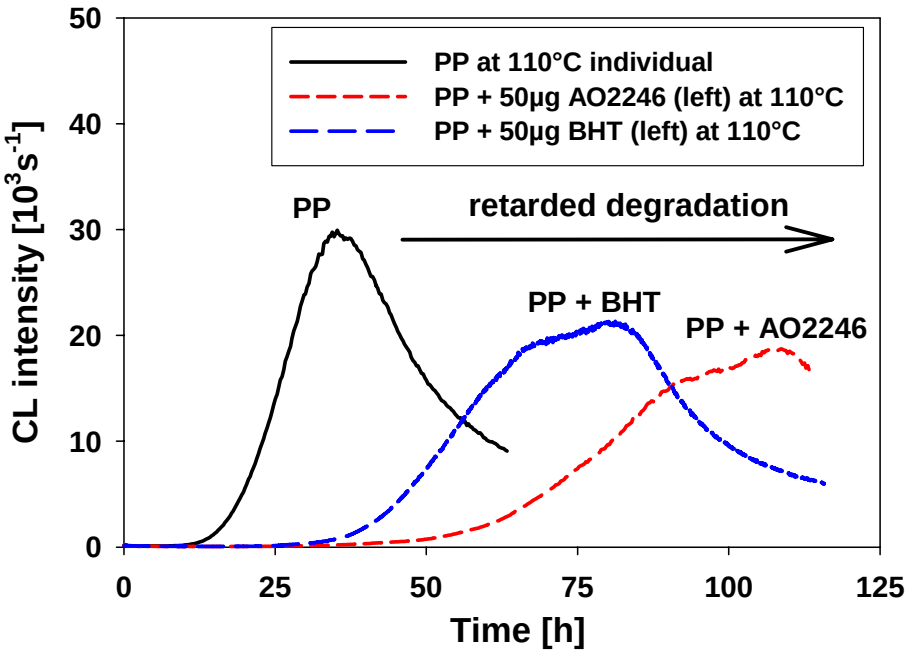

- BHT more volatile, but appears less effective
- Adsorption to target ?

Evidence for transfer of antioxidant, remote inhibition

Transfer of inhibitious species (AO)

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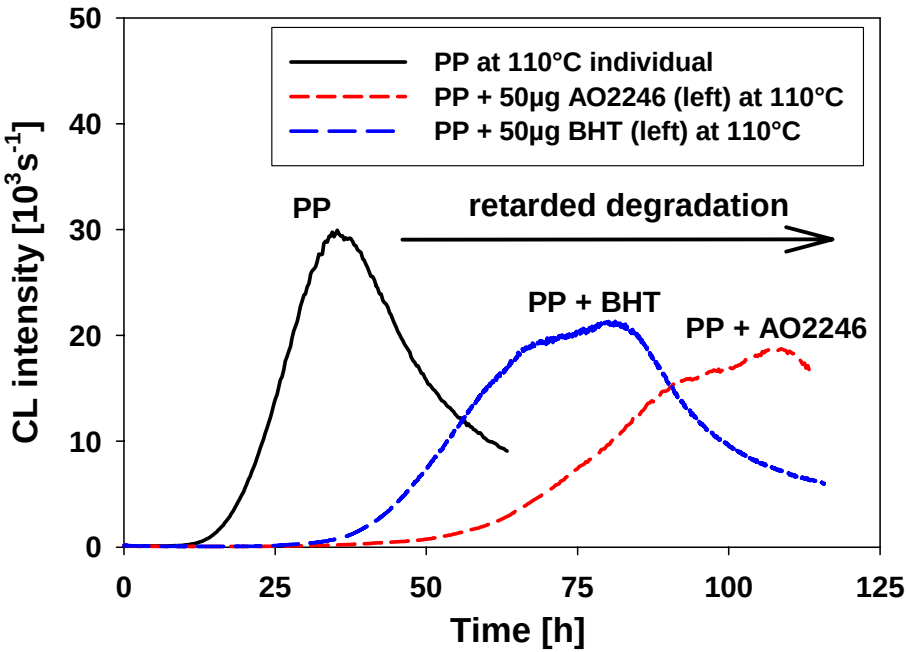
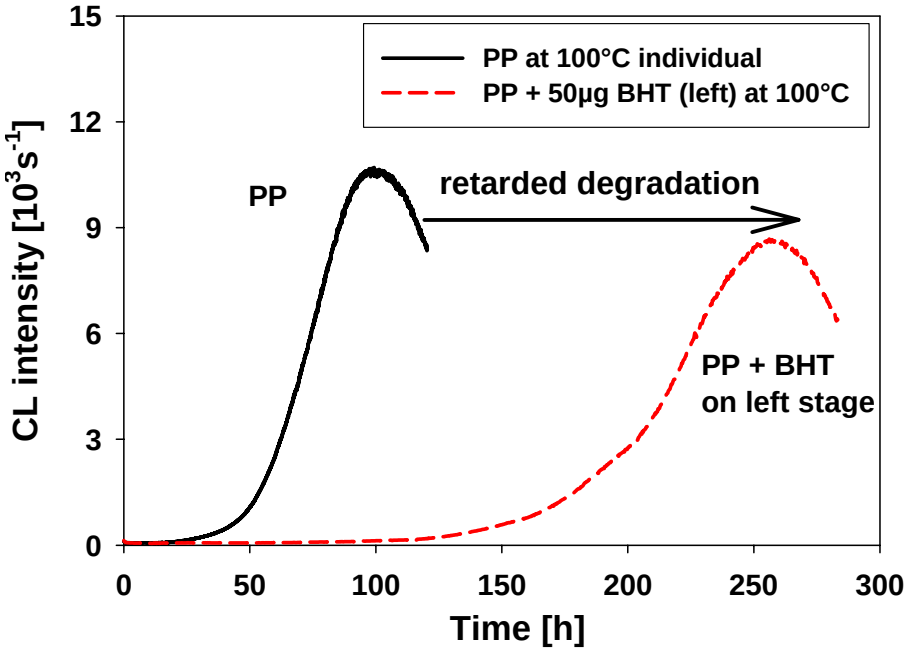


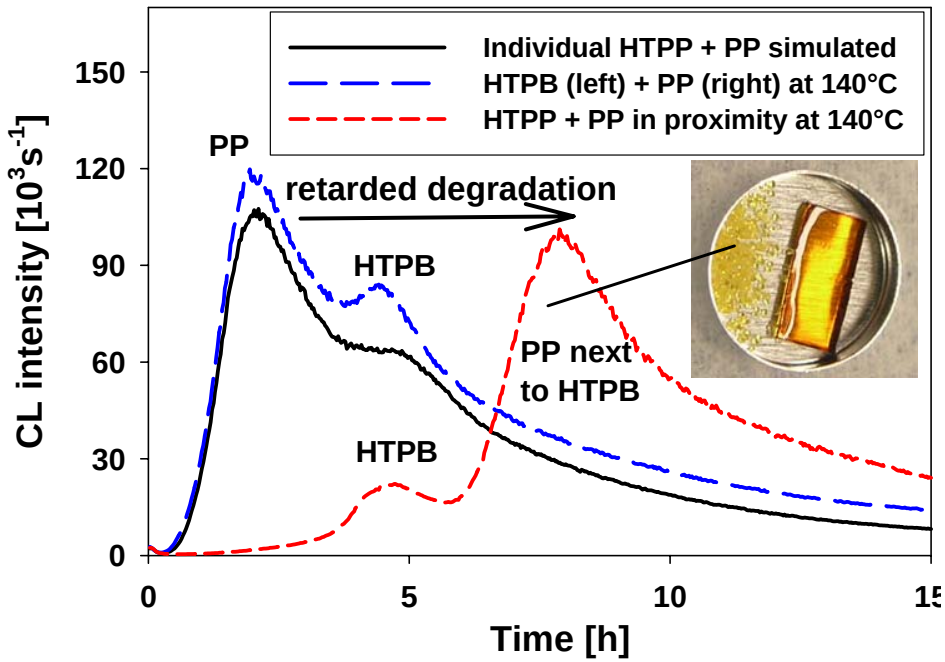


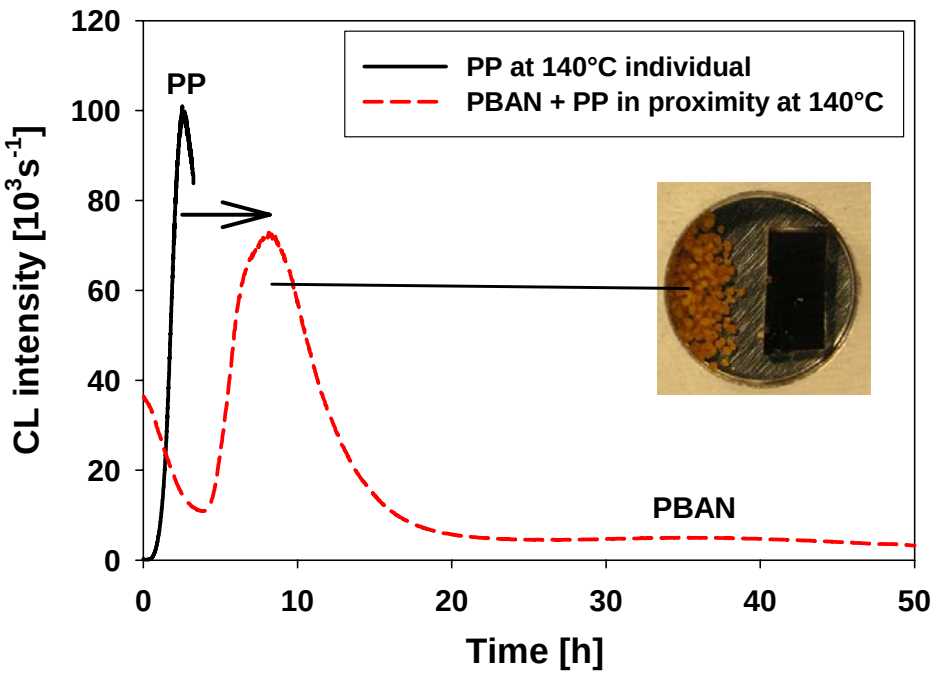
- BHT transfer and inhibition effective at lower T

Evidence for transfer of antioxidant, remote inhibition

AO transfer from stabilized materials

- Model experiment: Combined aging of elastomers with PP
- Antioxidant is transferred from the elastomer (50 µg total AO)
- Results in inhibition, but only when samples are closer





Volatile AO from Material A can inhibits degradation in B
But separation and available amounts for transfer are critical

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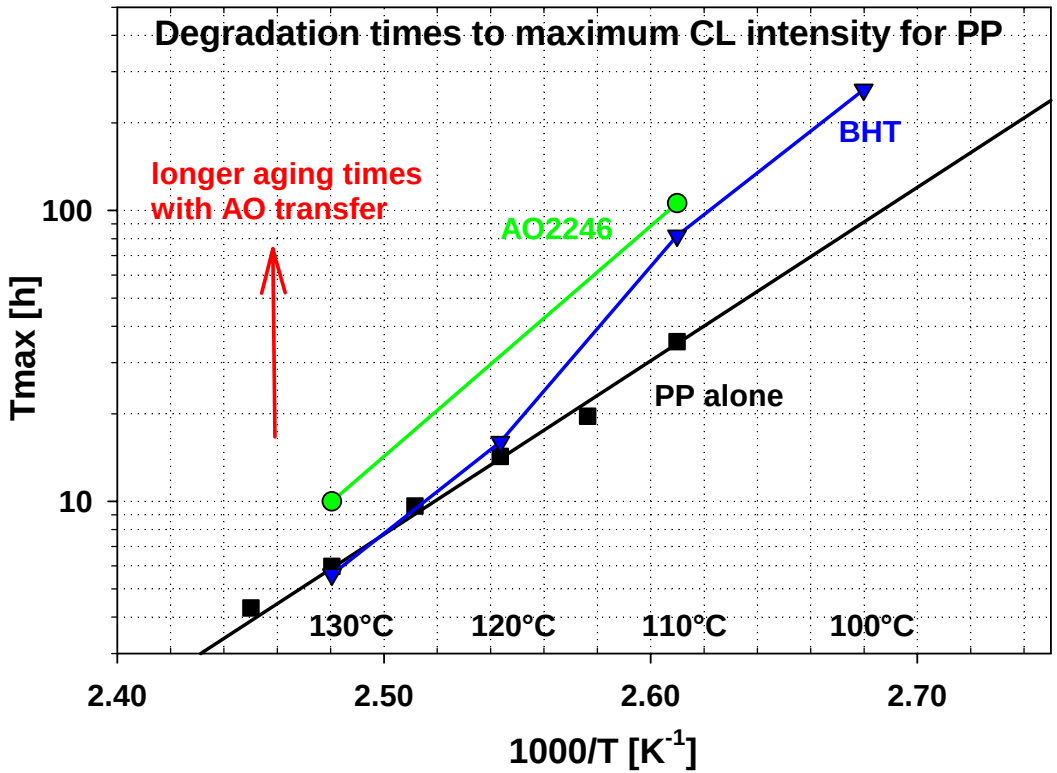
Efficiency of transfer processes

- Most volatile peroxides not efficient
- Critical balance between volatility and adsorptivity
- Low M_w compounds may escape easier
- Higher M_w species may adhere better to target
- Higher M_w AO compound more effective remote inhibitor



Transfer efficiency is a complex issue

Conclusions and impact

- Designed and built novel sensitive instrumentation to probe fundamental processes in polymer degradation
- Infection can lead to shorter lifetimes and occur remotely
- Metal ion contamination can equally lead to initiation
- Observations would be difficult to predict via materials modeling
- Demonstrated for the first time that polymers can be infectious
- Antioxidants can also be transferred and result in inhibition
- Effectiveness of transfer depends on volatility
- Remote infection and inhibition has been demonstrated

- **Polymer materials can clearly interact remotely**

Acknowledgements

Slawomir Karczewski and Paul Bentley at UNM
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