

Study on the Thermal Degradation of Polyoxymethylene by Thermogravimetry–Fourier Transform Infrared Spectroscopy (TG–FTIR)

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ABSTRACT: Thermal degradation behaviors of polyoxymethylene in nitrogen are systematically studied by Thermogravimetry–Fourier Transform infrared spectroscopy (TG–FTIR). Two primary degradation mechanisms are definitely determined by the production of formaldehyde and carbon monoxide collected from successive FTIR spectrum. First, POM tends to split off formaldehyde starting at unstable chain-ends, then random chain scission occurs at elevated temperature, and several related reactions possibly occur during the

degradation process. The results prove that during the degradation, formaldehyde is the predominant product, and therefore polyether as the stabilizers used can greatly improve the degradation temperature of POM in the initial stage, and consequently effectively inhibit the thermal degradation of POM. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3085–3092, 2006

Key words: polyether; TG-FTIR; degradation

INTRODUCTION

Polyoxymethylene (POM) is an important engineering plastic consisting of main chains of repeating carbon–oxygen bonds in the form of oxymethylene units (OCH_2). It offers an excellent balance of high strength and stiffness as well as good chemical resistance. Although POM possesses desirable properties, it is inherently unstable and readily undergoes thermal degradation. Earlier data^{1,2} shows that POM having unstable oxymethylene chain segments tends to follow an “unzipping” degradation with evolution of formaldehyde molecules. To reduce the tendency, an approach of copolymerization by the occasional incorporation of C–C bonds into the main chain has been developed. For additional stability, commercial products of POM copolymers are subjected to thermal treatment to modify the unstable hemiformal end group ($\text{O–CH}_2\text{OH}$) to a stable hydroxyethyl ether ($\text{–CH}_2\text{CH}_2\text{OH}$), and some necessary additives such as thermal stabilizers are also in use to achieve further stabilization.

The close relationship between degradation and stabilization for POM is interesting, while mechanisms concerned remain to be discussed.^{3–5} Since 1960s, the commercial exploitation, a great deal of study on thermal degradation behaviors of POM has been undertaken primarily by the method of TG, and the weight loss of POM is monitored under a constant heating rate during degradation by such a conventional thermoanalytical technique. A limitation to this technique, however, is that it cannot identify the degradation products. So some aspects of mechanisms in thermal degradation, though studied to a great extent, are merely deduced by the kinetics and degradation rate obtained from TG,^{2,6} and few investigations are made on the basis of degradation product. Recently, a comparatively new method of Thermogravimetry–Fourier Transform infrared spectroscopy (TG–FTIR) used in identifying degradation products of polymer materials is available in the literatures.^{7–9} In TG–FTIR, the gases evolved during thermal degradation can be analyzed simultaneously by FTIR. As proposed, an obvious advantage of TG-FTIR is that it can make the degradation study convenient and provide useful and convincing information about structure changes, which are not obvious through NMR or FTIR analysis,⁹ and therefore helps in understanding the degradation mechanism.

In this work, a detailed study of the thermal degradation for two types of polyoxymethylenes, the unstabilized and the stabilized by polyether, was conducted by TG–FTIR in nitrogen. The degradation mechanisms

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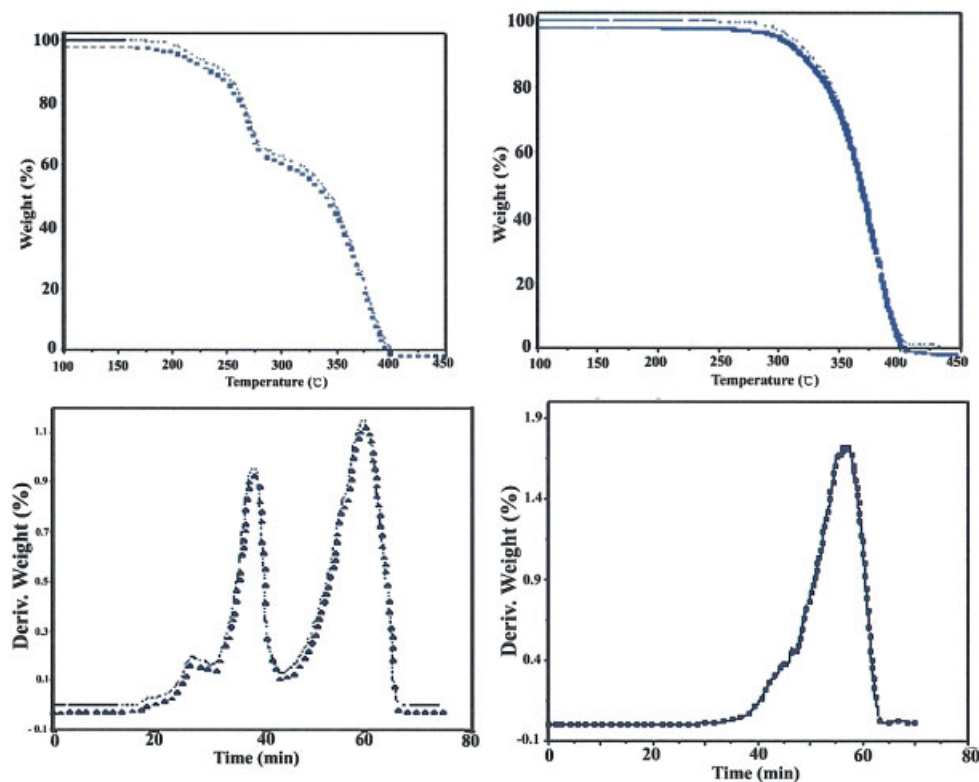


Figure 1 TG and DTG curves of POMs obtained in nitrogen atmosphere, with heating rate $5^{\circ}\text{C min}^{-1}$. Left, unstabilized POM. Right, stabilized POM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

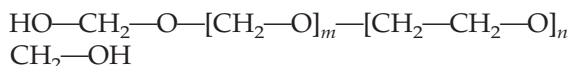
for POM are proposed and the effects of stabilizers on degradation processes are also investigated by the analysis of the degradation product detected by the infrared spectroscopy.

EXPERIMENTAL

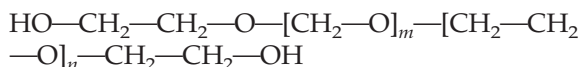
Materials

Polyoxymethylene copolymers used in this study comprised the following:

- unstabilized POM powder (melt index, 9 g/10 min), which did not undergo thermal post-treatment and has unstable hemiformal ends. The main chain structure is shown as follows:



- The stabilized commercial POM with polyether as stabilizers (melt index, 9 g/10 min). The molecular structure is shown as follows:



Both materials were kindly supplied by Yunnan Natural Gas Chemistry Co. Ltd.

Instrumental

TG-FTIR measurements were carried out by using a TGA-2950 instrument from TA Company, coupled with a Magna-75 FTIR spectroscopy. The TG instrument is linked to the heated gas cell of the FTIR instrument by means of a heated transfer line, and gases evolved from TG can be transferred into FTIR through the line by a suitable gas flow.

TG measurements were performed using samples of about 10 mg at a low heating rate of $5^{\circ}\text{C min}^{-1}$. The atmosphere was nitrogen, with a flow rate of 50 mL min^{-1} . Each spectrum was recorded in FTIR every 30 s, with a resolution of 2 cm^{-1} .

All samples were dried in a vacuum oven at 80°C for 2 h before test.

RESULTS AND DISCUSSION

Degradation of unstabilized polyoxymethylene

Figure 1 presents TG and DTG curves of the two types of POMs in the temperature range $100\text{--}450^{\circ}\text{C}$. For unstabilized POM, the TG thermogram in Figure 1 clearly shows that more than one process occur during degradation. According to the three maximum rate peaks in DTG curve, the whole degradation process

TABLE I
TG-FTIR Analysis for Unstabilized POM

	Stage 1	Stage 2	Stage 3	Stage 4
Time (min)	0-16	16-31	31-44	44-66
Temperature range (°C)	0-158	158-233	233-298	298-408
Residue (%)	100-99.97	99.97-92.56	92.56-62.66	62.66-0.50
Weight loss (%)	0.03	7.41	29.90	62.16
V_{\max} (%/°C)		0.19	0.95	1.15
T_{\max} (°C)		211	270	375

T_{\max} , the temperature at the maximum degradation rate; V_{\max} , the maximum degradation rate.

can be divided into four stages. The data obtained by TG are listed in Table I. The IR spectrum of the evolved gases for each stage is shown in Figure 2, and Table II lists the characteristic absorption bands of gases detected by FTIR spectroscopy.

The first stage during the early 16 min shows no significant decomposition, and only 0.03% weight loss is observed by TG. The IR spectrum in this stage shows bands H_2O at 1630 cm^{-1} and around 3400 cm^{-1} , which were associated with the water involved in POM. As the IR spectrum from 1800 to 1700 cm^{-1} was magnified in Figure 3, a minor absorption appears at 1745 cm^{-1} , corresponding to the formaldehyde molecule, the degradation product of hemiformal end groups. The results suggest that an initial weight loss occurs from the release of water and decomposition of unstable chain ends.

In the second stage, a very slow weight loss of 7.41% occurs from 150 to 233°C , passing the first maximum degradation rate at the 27th minute, with the value of $0.19\%/^\circ\text{C}$. No significant change is observed in IR spectrum, except an enhancement in typical formalde-

hyde bands. In this case, formaldehyde seems to be the only product. As unstabilized POM has unstable hemiformal ends ($-\text{CH}_2\text{OH}$) from which formaldehyde molecules are easily lost, and the production of formaldehyde is most likely to arise from chain-ends degradation.

Degradation in the third stage is so rapid as to for 30% weight in loss to occur within 30 min. The second maximum rate of $0.95\%/^\circ\text{C}$ is achieved at 270°C . IR spectrum indicates that bands at 2800, 1745, and 2300 cm^{-1} are intensified and the most important result is that a new band assigned to carbon monoxide appears at $2200\text{--}2000\text{ cm}^{-1}$, revealing another different mechanism of main chain scission occurring in this stage.

The main degradation occurs in the last stage. Above 298°C , the rate of weight loss increases dramatically to a maximum of $1.15\%/^\circ\text{C}$ at 375°C , resulting in the weight loss of 62.16%. In addition to the intensified adsorption of formaldehyde and carbon monoxide, a very small band at 1033 cm^{-1} is detected (see Fig. 4), which presents the existence of methanol. However, it is difficult to determine the formation of methyl for-

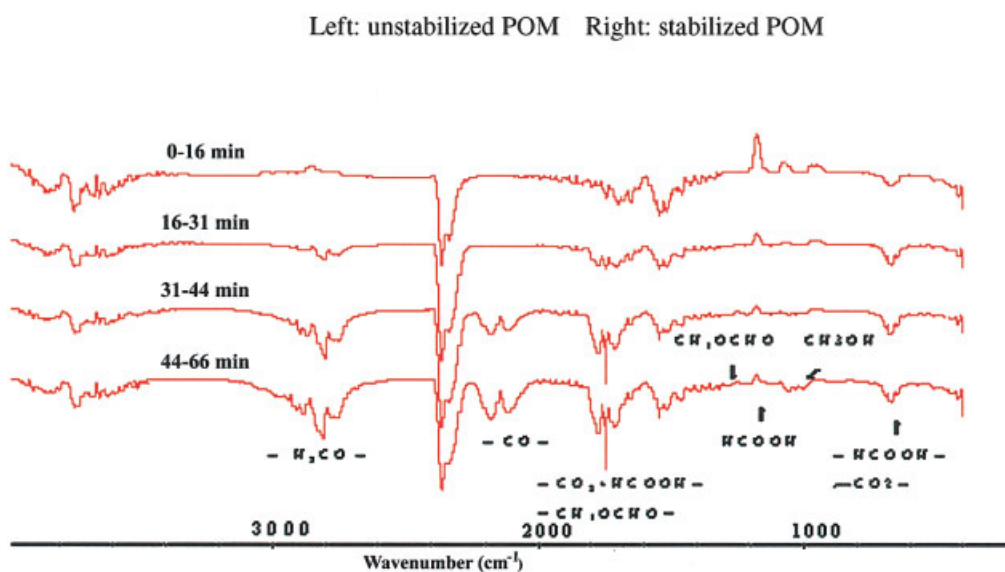


Figure 2 Infrared spectrum of the evolved gases for the unstabilized POM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Characteristic IR Absorption Bands of the Evolved Gases

Molecular formula	Signature (cm^{-1})
H_2CO (formaldehyde)	around 2800, 1745
CO (carbon monoxide)	2200–2000
HCOOH (formic acid)	1105
CH_3OH (methanol)	1033
CH_3OCHO (methyl formate)	1755, 1209
H_2O	around 3400, 1630

mate, because its characteristic absorption at 1755 and 1209 cm^{-1} are overlapped by the strong bands nearby. Figure 4 also shows that there is no appearance of formic acid at 1105 cm^{-1} during the whole degradation.

Degradation of the stabilized pom

As shown in Figure 1, the TG curve of the stabilized POM follows an S-shape correlation, indicating a single-step in thermal degradation. At a region during 30 and 50 min, a very slow weight loss appears before the main decomposition in DTG; consequently, three stages for degradation can be determined, as shown in Table III. Figure 5 shows the related IR spectrum in each stage.

Compared with the unstabilized powder, the stabilized POM exhibit good heat resistance at much higher degradation temperature. For the first stage, only 0.3% weight loss occurs within 30 min when temperature reaches 245°C . Gaseous components detected by IR include H_2O and low amount of H_2CO as shown in Figure 5. The vaporized formaldehyde

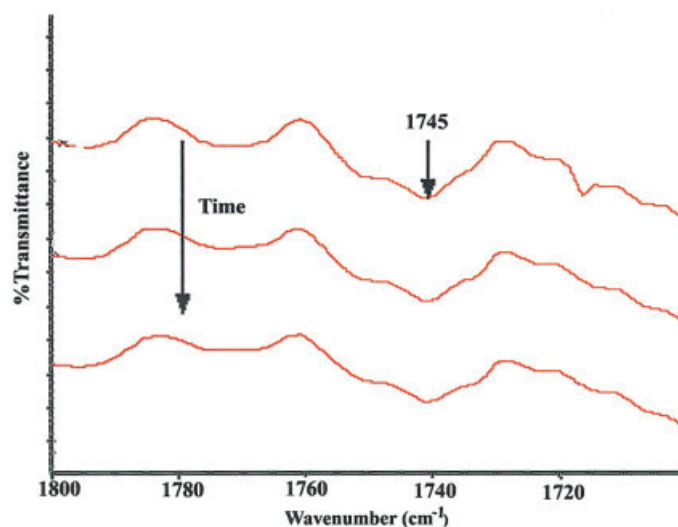


Figure 3 Infrared spectrum from 1700 to 1800 cm^{-1} for the evolved gases of the unstabilized POM at the degradation stage 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

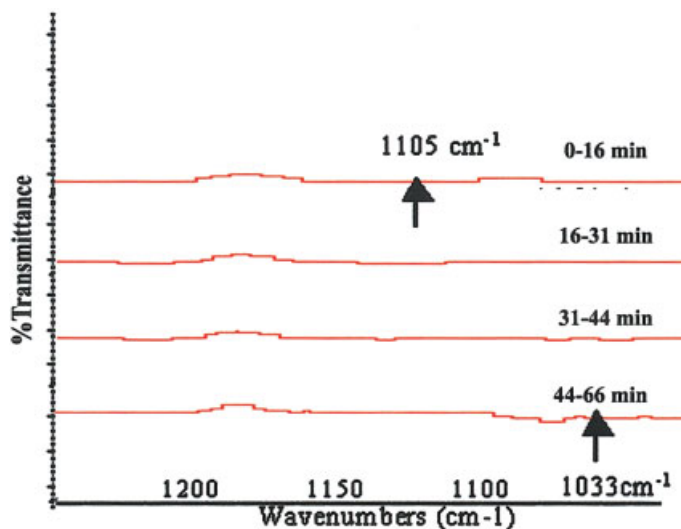


Figure 4 Infrared spectrum from 1000 to 1250 cm^{-1} for the evolved gases of the unstabilized POM during the degradation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Analysis of TG-FTIR for the Stabilized POM

	Stage 1	Stage 2	Stage 3
Time (min)	0–30	30–50	50–70
Temperature (°C)	0–245	245–345	345–445
Weight remaining (%)	100–99.71	99.71–78.08	78.08–0.60
ΔW_{loss} (%)	0.29	21.63	77.48
V_{max} (%/°C)			1.731
T_{max} (°C)			

T_{max} , the temperature at the maximum degradation rate;
 V_{max} , the maximum degradation rate.

would be accounted for the decomposition of the limited chain-ends remaining after thermal treatment. The IR spectrum from 1700 to 1800 cm^{-1} was magnified, as displayed in Figure 6.

The second stage presents a 21% weight loss in 20 min, with intense H_2CO absorptions at 2800 and 1745 cm^{-1} , respectively, in the corresponding spectrum. The typical bands at 2200–2000 cm^{-1} are attributed to the formation of CO as a demonstration of the chain-cleavage mechanism.

The main decomposition occurs mainly in the third stage, during which the absorption bands are greatly intensified as temperature increases, particularly the remarkable enhancement of H_2CO absorptions. From the magnified IR spectrum in Figure 7, a minor CH_3OH band at 1033 cm^{-1} and an extremely small absorption at 1105 cm^{-1} for HCOOH absent from the unstabilized copolymer are observed. However, the existence of CH_3OCHO cannot be confirmed yet for the same reason explained.

Degradation mechanisms

To make an effective comparison of degradation behaviors between the unstabilized and the stabilized POMs, the successive FTIR spectra of gases

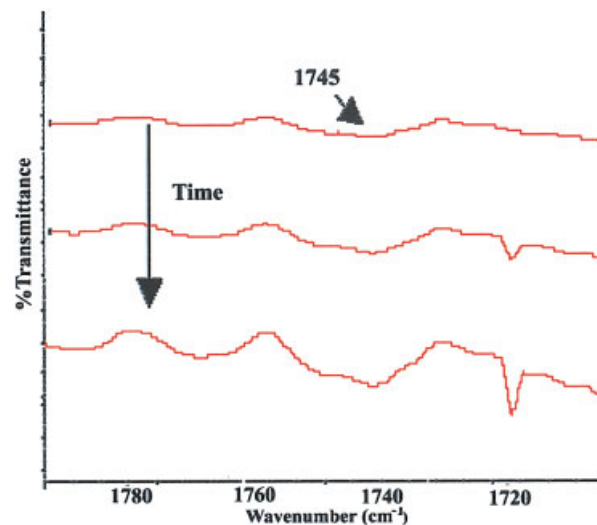


Figure 6 Infrared spectrum from 1700 to 1800 cm^{-1} for the evolved gases of the stabilized POM at the degradation stage 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

evolved during the whole degradation for both POMs are also shown in Figure 8, from which two significant mechanisms of POM degradation can be obtained.

First remarkable evolution of formaldehyde (H_2CO) observed at the initial stage of degradation for the unstabilized POM proves the fact that POM tends to split off formaldehyde starting at unstable chain-ends. This behavior has been described in early publications^{2,10,11} as a stepwise process until the thermally unstable ($-\text{CH}_2\text{OH}$) groups is unzipped into the stable ($-\text{CH}_2\text{CH}_2\text{OH}$) end groups. This tendency for the stabilized POM, which undergoes a thermal treatment to remove most of the unstable end groups, is obviously reduced. The chain-ends decomposition mechanism discussed above can be displayed as follows:

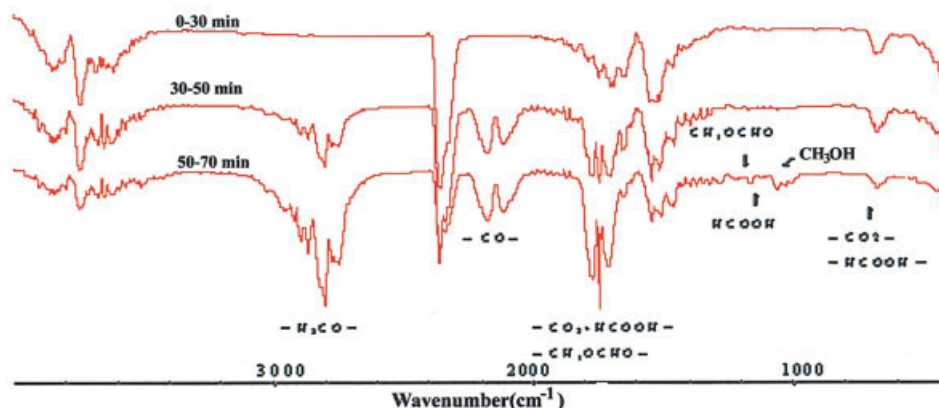


Figure 5 Infrared spectrum for the evolved gases of stabilized POM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

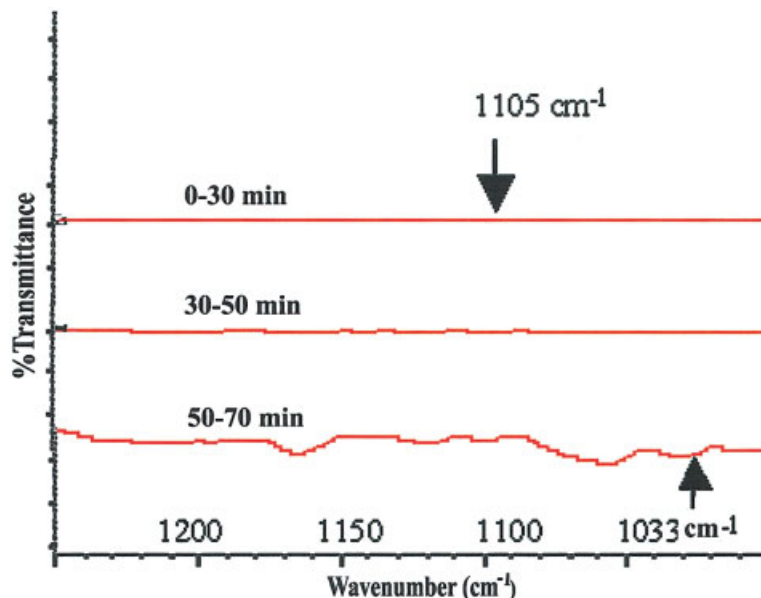
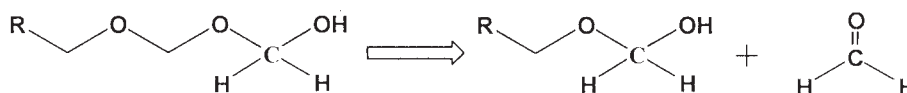


Figure 7 Infrared spectrum from 1000 to 1250 cm^{-1} for the evolved gases of the stabilized POM during the degradation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Then, the random chain scission occurs at elevated temperature, resulting in a sudden acceleration in degradation. As seen in Figure 8, besides the appearance of carbon monoxide bands at 2200–2000 cm^{-1} , both absorption of formaldehyde (H_2CO) and carbon monoxide in this period are intensified greatly with increasing temperature, until the degradation up-

surge. This acceleration is quite likely attributed to the random scission of main chains, which increases the concentration of hemiformal end groups. As the decomposition starts at unstable end groups, the degradation rate will rise rapidly. Another reason for the acceleration has been emphasized by Dudina⁴ that besides the random splitting of the chains, there is also

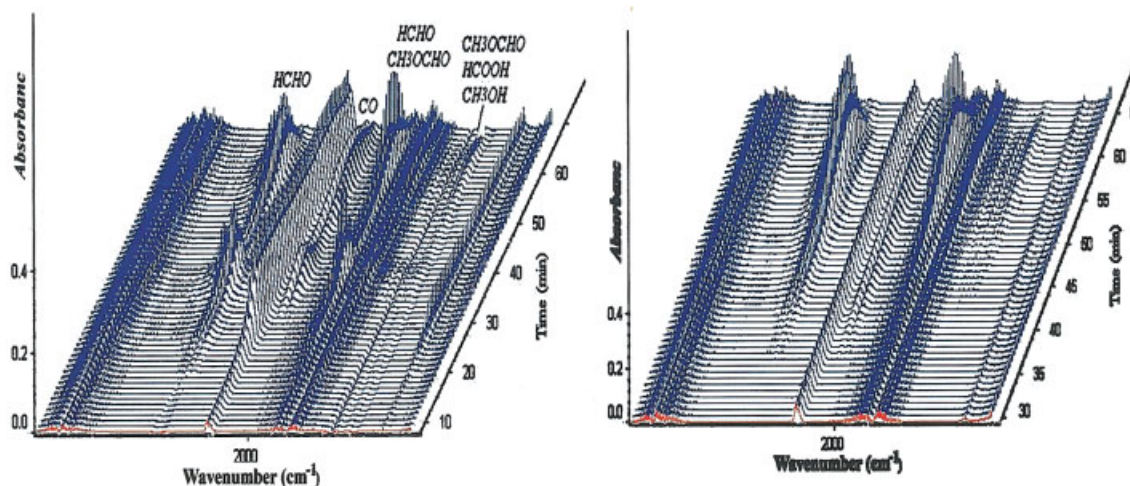


Figure 8 Successive FTIR spectra of gases evolved during thermal degradation of POM as a function of time. Left, unstabilized POM. Right, stabilized POM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

As shown in Table IV, POM, which contains stabilizers, is more resistant to thermal degradation, so that the weight loss within 40 min is only 2.38%, ten times less than that of unstabilized POM. Although the modified terminal groups in stabilized POM, to some extent, can prevent chain-ends decomposition at a lower temperature, stabilizers would play the most significant role to reduce the tendency for degradation, by consuming formaldehyde when POM is subjected to long-time heating.

The results demonstrate that in nitrogen atmosphere, stabilizers enable suppression of the thermal degradation effectively and enhance the resistance of POM to degradation.

CONCLUSIONS

With TG-FTIR analysis of the stabilized POM in comparison with the unstabilized one, thermal degradation behaviors of POM are investigated. Two primary mechanisms of thermal degradation are definitely deduced: the depolymerization from chain-ends, and random chain scission. During the degradation, considerable amount of formaldehyde, carbon monoxide,

and limited amount of methanol are produced, among which formaldehyde is proved to be the predominant product, and under inert atmosphere, the degradation of POM would be retarded in the presence of formaldehyde acceptors.

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