Plasma Polymerization of Organoisothiocyanates. II. Structure of Polymer Film

G. CZEREMUSZKIN, A. M. WRÓBEL, and M. KRYSZEWSKI

Polish Academy of Sciences, Center of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland

SYNOPSIS

Methyl-, n-propyl-, allyl-, and phenyl isothiocyanates (MITC, PITC, AITC, and PHITC respectively) were polymerized in an RF (13.56 MHz) plasma electrodeless flow system. The plasma produced polymers were characterized using IR, GPC, GC/MS, and direct pyrolysis mass spectrometry (DPMS) techniques. The solubility tests and chromatographic examinations of the polymers revealed a small soluble fraction which contained a mixture of oligomers with a predominance of dimers and trimers. Molecular structure of the components of these fractions, identified by GC/MS, suggests fragmentation of the monomers to reactive fragments: ˙RSCN, ˙RCN, R˙, ˙CN (in the case of MITC, PITC, AITC) and ˙ArNCS, PhS˙, Ph˙, ˙CN (in the case of PHITC). The DPMS data, being generally consistent with IR and GS/MS results, proved the presence in the polymers of sulfide, polysulfide, thiocarbonyl ($-CS-S-$ and $-S-CS-S-$) groups, and molecular sulfur S_8. Elementary plasma reactions involved in the formation of the observed structural units are proposed.

INTRODUCTION

Plasma polymerized (PP) organoisothiocyanates are, due to their content of nitrogen and sulfur,[1] an interesting class of polymeric materials, particularly in terms of their electrical properties.[2,3] However, in the case of plasma polymers, an important problem, often difficult to resolve, is to find a reasonable correlation between the properties of the polymer and its chemical structure or composition. The difficulties associated with finding such a correlation mainly arise from the complexity of plasma polymerized materials and the resulting inability of precisely determining their structure. Plasma polymers, in contrast to their conventional counterparts, are generally known as materials of highly crosslinked, branched, and irregular structure. Owing to the small quantity of the polymer produced in the plasma polymerization process and its usually poor solubility in organic solvents, structural studies of plasma polymerized materials need analytical techniques more sophisticated than those used for conventional polymers. Most of these methods have been recently described in our review article.[4]

The current paper contains the results of the structural studies carried out for plasma polymers produced from methyl-n-propyl-, allyl-, and phenyl isothiocyanates (MITC, PITC, AITC, and PHITC, respectively) as well as of the low molecular weight fraction extracted from the polymers. Knowledge of the molecular structure of compounds present in this fraction appears to provide valuable information not only on the structure of plasma polymers but also on the mechanism of elementary plasma reactions which may contribute to the polymerization process.[2,5-9] The plasma polymers were analyzed by infrared spectroscopy, and direct pyrolysis mass spectrometry (DPMS), whereas the low molecular weight fraction was subjected to gel permeation (GPC) and gas chromatography/mass spectrometry (GC/MS) examinations. It is noteworthy, that DPMS is a novel, hitherto unreported technique with respect to analysis of plasma polymers. This technique entirely prevents the formation of undesirable secondary pyrolysis products, due to the fact that pyrolysis of the sample takes place directly in the mass spectrometer. Based on the structural data,

elementary plasma reactions of the organoisothio-cyanates are postulated.

EXPERIMENTAL

Monomers MITC, PITC, AITC, and PHITC (Fluka, ICN) were purified by distillation and degassed by freezing-thawing evacuation cycles, prior to plasma polymerization.

Plasma polymerizations were carried out in a tubular reactor, inductively coupled with an RF (13.56 MHz) power source. Detailed description of this apparatus has been reported previously.[1] Polymer films were deposited on Corning 7059 glass pellets placed in the reactor at a distance of 45 cm from the origin of the tube, using the initial monomer vapor pressure p_i = 6.7 Pa, flow rate F = ~ 4 sccm, an output power P = 100 W.

Infrared spectra of the polymer films were recorded on Perkin–Elmer 457 and Specord M 80 IR spectrometers by using the ATR, MIR, condensed beam, and transmission techniques. For the ATR and MIR techniques, polymer films were deposited on a Corning glass coated with an Al layer and on Al foil, respectively. For the condensed beam technique a piece of polymer film removed from Al foil was used, and for the transmission technique KBr pellets were used.

The DPMS analysis was performed on a LKB 2910 mass spectrometer. The polymer samples were heated directly in the mass spectrometer within a temperature range 300–520 K using a constant heating rate of 10 K/min. The mass spectra were recorded after every 10 K increase in the temperature and renormalized to obtain the absolute intensity of particular ion peaks.

Low molecular weight products extracted from polymer films with methanol, benzene, acetone, and chloroform as well as collected in liquid N_2 cold trap were analyzed by the GC/MS technique. The products were separated in a LKB gas chromatograph equipped with a flame ionization detector and a 2.7 m × 2 mm stainless steel column filled with 10% OV 101. The separated products were then analyzed by the mass spectrometer.

The GPC chromatograms of low molecular weight fractions extracted from the polymers with tetrahydrofuran, were recorded on a Varian gel permeation chromatograph.

RESULTS AND DISCUSSION

Infrared Spectroscopy

Figure 1 shows the IR absorption spectra of (a) PP–MITC, (b) PP–PITC, (c) PP–AITC, and (d) PP–PHITC. The particular absorption bands were identified according to the literature data,[9-14] and their assignments are presented in Table I. Referring to Figure 1 and Table I, one may note numerous spectral features characteristic of the investigated plasma polymers. The absorption band at 3400 cm^{-1} (marked with the letter A) corresponds to the stretching vibration of N—H in thioamides and amides. The latter compounds are probably produced via post-plasma reaction of trapped radicals
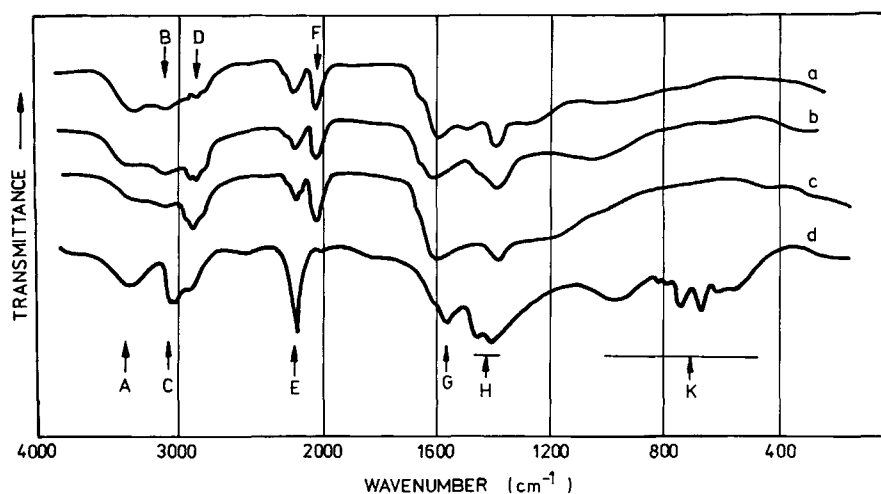
Figure 1 IR spectra of plasma polymers from (a) MITC, (b) PITC, (c) AITC, and (d) PHITC. The most important absorption bands are marked with arrows and letters.

Table I Infrared Absorption Bands Characteristic of Examined PP–organoisothiocyanates

Symbol[a]	Absorption Band (cm^{-1})				Assignment
	PP–MITC	PP–PITC	PP–AITC	PP–PHITC	
A	3400	3400	3300	3360	N–H
B	3200–3100	3200–3100	3200	—	N–H
C	—	—	—	3050	C–H (aromat.)
	—	—	—	3020	
D	2960	2960	2960	2980–2850	C–H (aliphat.)
	2920	2920	2920		
	2870	2870	2870		
E	—	—	2240	—	$-CH_2-C{\equiv}N$
	2230	2230	—	—	$\diagdown C=C-C{\equiv}N$
	—	—	—	2220	aryl$-C{\equiv}N$
	—	—	2200	—	$\diagdown N-C=C-C{\equiv}N$
	2190	2190	—	—	$\diagdown N-C{\equiv}N$
	—	—	2160	—	$-S-C{\equiv}N, -N=C$
F	2030	2040	2040	2040[b]	$\diagdown C=C=N-$
G	1670	1660	1670	1600	$\diagdown C=C\diagup, \diagdown C=N-$
	1620	1620	1620	1580[b]	
H	1450	1500	1410	1480	$-S-R, =N-R,$ $R= -CH_3, -CH_2-,$ $-CH_2-C{\equiv}N$
	1400	1400	—	1430	
K	—	—	—	1000	aromatic ring vibr.
	—	—	—	800	
	—	—	—	760	
	—	—	—	700	

[a] Letters denote absorption bands according to Figure 1.
[b] Very weak.

which contained nitrogen atoms. The analogous band was observed in IR spectra of the hydrolysis products of the monomers, which consisted of the respective amides.[12] Band B in the range of 3200–3100 cm^{-1}, observed in spectra of PP–MITC, PP–AITC, and PP–PITC is assigned to the absorption of N—H in amidine groups. Amidines [—N=C(—NRH)—C—)] were the product of plasma conversion of ketenimine group (—N=C=C), existing, as it will be shown later, in the polymers mentioned above. This assignment seems to be reasonable, since band B does not appear in spectra of PP–PHITC in which ketenimine groups (the amidine precursor) were practically absent [Fig. 1, spectrum (d)]. The bands marked C

at 3050 cm^{-1} and 3020 cm^{-1}, seen in spectra of PP–PHITC and ascribed to the stretching vibration of aromatic C—H, prove the presence of aryl groups in this polymer. An aliphatic absorption band D at 2980–2850 cm^{-1} was related to the asymmetric and symmetric stretching modes of —CH$_2$— and —CH$_3$ groups. In the case of PP–PHITC, the presence of this band in the IR spectra proved the plasma fragmentation and partial aliphatization of the phenyl group in the monomer. The absorption band E in the 2240–2150 cm^{-1} region may arise from the stretching vibration of nitrile groups (—C≡N) bonded to different units as shown in Table I. The nitrile group, present in all investigated polymers, seems to be one of the most frequent and stable

plasma conversion products of the isothiocyanate substituent. The next band, F, in the range of 2030–2040 cm^{-1} was observed almost exclusively in the spectra of aliphatic isothiocyanates [Fig. 1, spectra (a) and (b)] and is attributed to the asymmetric stretching vibration of the ketenimine group.[10] Band G in the 1580–1670 cm^{-1} region is ascribed to the absorption of $\diagup\!\!\diagdown C{=}C\diagdown\!\!\diagup$ and $\diagup\!\!\diagdown C{=}N{-}$ groups, and presumably, of the carbonyl group in amides as well. Several bands denoted with letters H and K (as shown in Table I) are related to the absorption of the $-CH_2-$ and $-CH_3$ groups and aryl ring, respectively. The presence of the latter bands in the spectra of PP–PHITC proves, in conjunction with band C, the contribution of the aromatic rings to the structure of this polymer.

The most important information provided by the IR spectra is the absence of the absorption characteristic of the isothiocyanate group which observed in the spectra of the monomers as a very strong and broad band in the 2150–2050 cm^{-1} region. This evidently proves that the $-N{=}C{=}S$ group undergoes nearly complete fragmentation under plasma conditions.

Similar IR analyses have also been performed on the extraction products of the investigated plasma polymers which were obtained with various solvents. The solubility tests showed that the polymers, directly after deposition, were slightly soluble in acetone, dimethylformamide, tetrahydrofuran, chloroform, dimethylsulfoxide, and dioxane; much less

soluble in n-hexane, benzene, and diethyl ether; and practically insoluble in aliphatic alcohols and water. The IR spectra of both insoluble and soluble fractions of the polymers separated by the extraction in the mentioned organic solvents, were similar, as exemplified in Figure 2 which presents the IR spectra of (a) PP–PHITC deposit, (b) its soluble fraction extracted with chloroform, and (c) insoluble residue. This suggests that the low molecular weight compounds trapped in the polymers as well as the cross-linked fraction are composed of the same structural units.

IR spectroscopy has been used to evaluate the effect of atmospheric aging upon the structure of plasma polymer films. The IR spectra recorded after various durations of exposure to the ambient revealed that the aging process resulted only in an increase of the absorption from the amide groups. After aging for about 100 h the polymers became completely insoluble in organic solvents.

Gel Permeation Chromatography

The GPC examination carried out for soluble fractions separated from the polymers by extraction in tetrahydrofuran provided information on the number of components and their molecular weights. As revealed by the GPC data, this fraction appeared to be most abundant in the case of PP–PHITC. The GPC chromatogram of the tetrahydrofuran extract of this polymer and standard polystyrene solution, used for evaluation of the molecular weight distri-
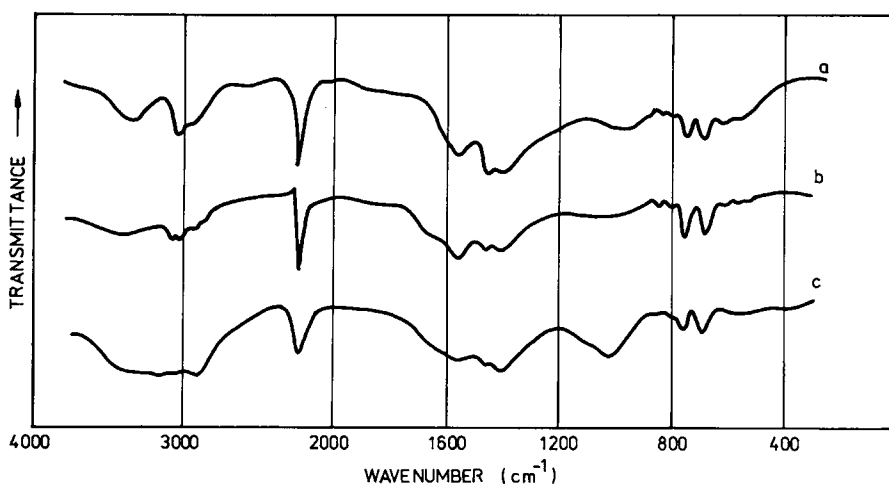
Figure 2 IR spectra of (a) PP–PHITC as deposited, (b) its soluble fraction extracted with chloroform (the spectrum of the material was taken after evaporation of the solvent), and (c) insoluble residue.
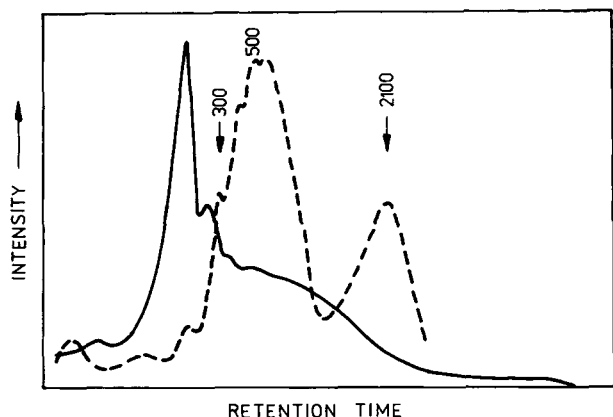
Figure 3 GPC spectrum of soluble fraction of PP–PHITC (continuous line) and polystyrene standard (dashed line) obtained for the solution in tetrahydrofuran.

bution, are presented in Figure 3. From these comparative GPC chromatograms, it may be concluded that the soluble fraction of PP–PHITC contains a mixture of oligomers with molecular weights not exceeding 800–1000 and with a predominance of dimers and trimers.

Gas Chromatography/Mass Spectrometry

Valuable information on the structure of the plasma polymers may be obtained by GC/MS examination of their low molecular weight fractions. This combined technique due to its high resolution seems to be powerful analytical tool, as has been demonstrated for pyrolysis products[6-8] and extraction products[5,9] of organosilicon plasma polymers.

Figure 4 shows a gas chromatogram of the benzene solution of low molecular weight fraction extracted from PP–PHITC. The identified compounds corresponding to the respective GC peaks are listed in Table II, which also contains the GC/MS results for the remaining plasma polymers. The identification was based mainly on MS data in the literature[15,16] due to the difficulties in finding suitable standard compounds. However, in most cases the mass spectra of the analyzed compounds coincided well with those of the respective standards in the literature.

Data in Table II show that the soluble fractions of the investigated plasma polymers contain numerous plasma conversion products of the monomers, with molecular weights usually not higher than those of dimers. Further, a striking observation is that PP–PHITC appears to be much richer in low

molecular weight components than plasma polymers of aliphatic and olefinic isothiocyanates. Molecular structures of the compounds in Table II imply that plasma fragmentation of the monomers has occurred to form reactive fragments: ˙RSCN, ˙RCN, R˙, ˙CN (in the case of MITC, PITC, AITC) and ˙ArNCS, PhS˙, Ph˙, ˙CN (in the case of PHITC). Taking into account a predominant role of radicals in plasma polymerization[17] and the fact that the photolysis[18] and radiolysis[19] of organoisothiocyanates and organothiocyanates are known to be radical processes, our assumption of the radical nature of the reactive fragments seems to be justified. Recombination of radicals and their reactions with neutral molecules readily explains the formation of low molecular weight compounds detected by GC/MS. The elementary plasma reactions leading to the formation of the observed products will be discussed later.

Direct Pyrolysis Mass Spectrometry

The DPMS results obtained for all investigated plasma polymers are presented in Figures 5–7 which show the intensity of particular mass peaks as a function of pyrolysis temperature. The DPMS data on the sulfur fragmentation were similar for each investigated polymer, and are exemplified in Fig. 7(b) by the results obtained for PP–MITC.

The changes in the intensity of particular ion peaks with increasing temperature are shown in
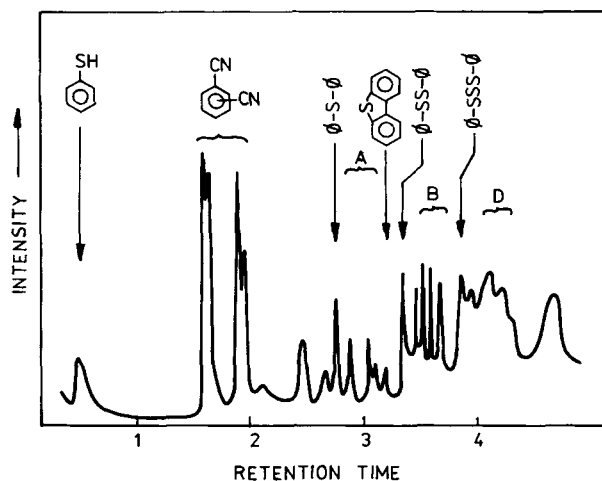
Figure 4 Gas chromatogram of the benzene solution of low molecular weight fraction extracted from PP–PHITC. The peaks marked with letters A and B correspond to the isomers of acridine and phenylbenzothiazole, respectively, and D to nonidentified dimers.

Table II Low Molecular Weight Compounds Identified by GC/MS in the Soluble Fractions of the Investigated Organoisothiocyanate Plasma Polymers

No.	Molecular Weight	Formula	Structure	Number of Isomers
	73		PP–MITC	
1	78	$C_4H_2N_2$	$N{\equiv}C{-}CH{=}CH{-}C{\equiv}N$	3
2	80	$C_4H_4N_2$	$N{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}N$	1
3	94	$C_5H_6N_2$	$H_2C{=}CH{-}NH{-}CH{=}CH{-}C{\equiv}N$	2
4	106	$C_6H_6N_2$	$N{\equiv}C{-}CH_2{-}CH_2{-}CH{=}CH{-}C{\equiv}N$	1
5	108	$C_6H_8N_2$	$N{\equiv}C{-}(CH_2)_4{-}C{\equiv}N$	1
6	129	$C_4H_7N_3S$		1
	97		PP–PITC	
1	67	C_4H_5N	$H_2C{=}CH{-}CH_2{-}C{\equiv}N$	1
2	101	C_4H_7NS	$C_3H_7{-}SCN$	2
3	135	$C_4H_9NS_2$	$HS{-}(CH_2)_3{-}\overset{H}{\underset{}{N}}{-}\overset{H}{\underset{}{C}}{=}S$	1
4	154	$C_5H_2N_2S_2$	$SCN{-}C_3H_2{-}NCS$ (?)	1
	95		PP–AITC	
1	67	C_4H_5N	$H_2C{=}CH{-}CH_2{-}C{\equiv}N$	2
2	99	C_4H_5NS	$C_3H_5{-}SCN$	2
3	103	C_7H_5N	⟨◯⟩$-C{\equiv}N$	1
4	168	$C_6H_4N_2S_2$	$(H_2C{=}C{=}N{-}\overset{S}{\overset{\|}{C}}{-})_2$	2
	135		PP–PHITC	
1	110	C_6H_5S	⟨◯⟩$-SH$	1
2	124	C_7H_8S	$CH_3{-}$⟨◯⟩$-SH$	1
3	128	$C_8H_4N_2$	$N{\equiv}C{-}$⟨◯⟩$-C{\equiv}N$	2
4	135	C_7H_5NS	⟨◯⟩$-NCS$; ⟨◯⟩$-SCN$	2
5	142	$C_6H_{10}N_2S$	aliphatic cmpd.	1
6	154	$C_{12}H_{10}$	⟨◯⟩$-$⟨◯⟩	1

Table II *(Continued)*

No.	Molecular Weight	Formula	Structure	Number of Isomers
	135		PP–PHITC	
7	155	$C_9H_5N_3$		5
8	162	$C_8H_6N_2S$		3
9	179	$C_{13}H_9N$		2
10	184	$C_{12}H_8S$		1
11	186	$C_{12}H_{10}S$		1
12	211	$C_{13}H_9NS$		3
13	218	$C_{12}H_{10}S_2$		2
14	226	$C_{13}H_{10}N_2S$		1
15	238	$C_{14}H_{10}N_2S$		3
16	243	$C_{13}H_9NS_2$		3
17	250	$C_{12}H_{10}S_3$		1
18	270	$C_{14}H_{10}N_2S_2$	Dimer[a]	3
19	270	$C_{14}H_{10}N_2S_2$	Dimer[b]	
20	295	$C_{15}H_9N_3S_2$	Dimer + CN – H	

[a] Base peak at m/e = 204.
[b] Base peak at m/e = 236.

Figures 5–7; these changes suggest that two types of processes occur in the mass spectrometer. The first process proceeding at low temperatures, is desorption of low molecular weight compounds which are trapped in the polymer matrix during polymerization. The second process taking place at higher temperatures, is associated with pyrolysis of the polymer.

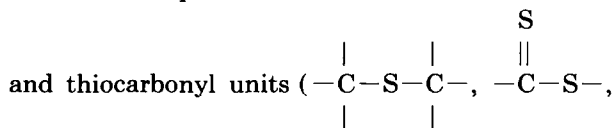In the first stage of heating, in the temperature range of 320–400 K, the evolution of molecular sulfur
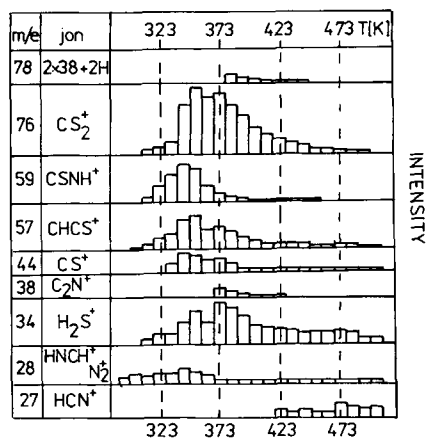
Figure 5 Intensity of the main ion peaks in the mass spectrum of PP–MITC as a function of pyrolysis temperature.

S_8 and carbon disulfide from each examined plasma polymer; dicyanoethene from PP–PITC and PP–AITC (Fig. 6); phenylbenzothiazole, acridine and dicyanobenzene from PP–PHITC (Fig. 7(a), is observed. These compounds were identified on the basis of the changes in the intensity of their parent and fragment ion peaks, by comparison of the DPMS data with the literature MS data[15,16] and with the results of GC/MS analysis of the respective plasma polymer extracts.
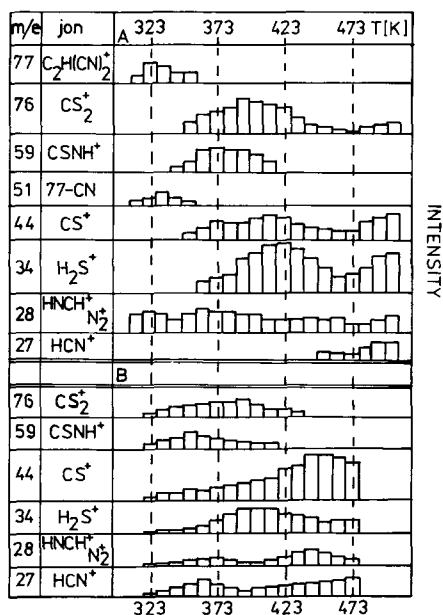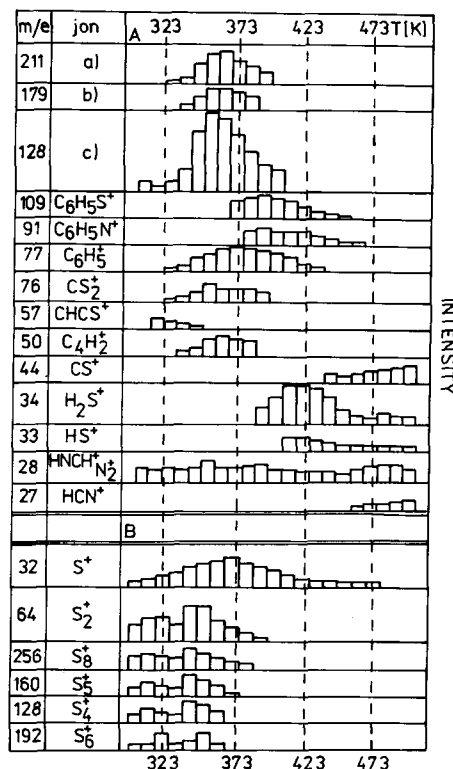

Figure 6 Intensity of the main ion peaks in the mass spectrum of (A) PP–PITC and (B) PP–AITC as a function of pyrolysis temperature.

The second process, developed in the temperature range of 450–500 K, is associated with the intense ion peaks for S^+, HS^+, H_2S^+, and CS^+ as well as HCN^+ which appear in the mass spectra of all examined polymers. Since these ions, were observed mainly at higher temperatures, it is reasonable to assume that they derive from the pyrolysis products of the polymers. The S^+, HS^+, H_2S^+, and CS^+ ions prove the contribution of the sulfide

and thiocarbonyl units (

$$
\begin{array}{ccc}
\text{S} & \text{S} & \text{S} \\
| & | & \| \\
-\text{C}-\text{S}-\text{C}-, & -\text{C}-\text{S}-, \\
| & |
\end{array}
$$

$$
\begin{array}{c}
\text{S} \\
\| \\
-\text{S}-\text{C}-\text{S}-
\end{array}
$$

) to the structure of plasma polymers, whereas the HCN^+ ion shows the presence of nitrile groups.

The change in the intensity of sulfur ions exemplified by the DPMS histograms in Figure 7(b), is accounted for by the presence in the polymer of two types of sulfur structures. The S^+ ion originates from the decomposition of the thiol, sulfide, or poly-

Figure 7 Intensity of the main ion peaks in the mass spectrum of (A) PP–PHITC and sulfur ion peaks (B) in the mass spectrum of PP–MITC as a function of pyrolysis temperature.

sulfide units, whereas, the S_2^+, S_4^+, S_5^+, S_6^+, and S_8^+ ions with the maximum intensity appeared at lower temperature with respect to S^+, are indicative of molecular sulfur, S_8. The latter finding is also confirmed by fragmentation patterns of S_8 reported in the literature.[16]

The DPMS results were consistent with those obtained by IR, and GC/MS techniques both of which also revealed the presence of nitrile, thioamide, amidine, and sulfide groups, as well as low molecular weight compounds in all investigated materials. The above findings show that DPMS is a good supplementary analytical method for the examination of plasma polymers, and in particular, of their insoluble fraction which dominates in these materials.

Elementary Plasma Reactions

On the basis of the GC/MS, DPMS, and IR studies the main elementary reactions involved in the formation of identified structures can be postulated. The isothiocyanate group, under influence of energetic UV radiation emitted by a plasma, may readily undergo isomerization to a thiocyanate unit according to the reaction:

$$R - NCS \xrightarrow{h\nu} [R - NCS]^* \rightarrow$$
$$[R - SCN]^* \xrightarrow{M} R - SCN \quad (1)$$
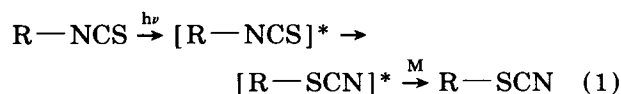
(where M denotes neutral molecule and R is an alkane, alkene, or phenyl group). The isothiocyanate-thiocyanate isomerization has been observed in solution as chemically, radiation-, and photoinduced reactions.[13] The bimolecular substitution or dissociative (ionic or radical) character of these reactions has been reported.[19,20] The mechanism via intimate ion pair has also been proposed.[21] However, in a plasma, isomerization seems to be a unimolecular reaction. The considered reaction is in good agreement with the presence of thiocyanate monomer derivatives in the low molecular-weight fraction of PP–PITC, PP–AITC, and PP–PHITC (see Table II).

The isomerization process may be associated with dissociation of the excited thiocyanate molecule to highly reactive thiyl and nitryl radicals:

$$[Ph - SCN]^* \rightarrow Ph - S^{\cdot} + CN^{\cdot} \quad (2)$$
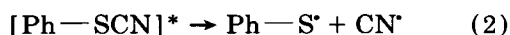
Reaction (2) seems to be the most important primary step in the plasma conversion process of PHITC that appears to produce relatively high amounts of thiophenol and diphenyl disulfide (Fig. 4). The presence of these compounds supports the formation of PhS species.

In the case of MITC, PITC, and AITC, elimination of the sulfur from the monomer molecule is considered to be the predominant primary step in the plasma conversion process. This is indicated by the numerous sulfurless conversion products of these monomers as described in Table II. The sulfur elimination reaction, photochemically induced, results in the formation of isonitrile group and a reactive sulfur atom:[18]

$$R - N = C = S \xrightarrow{h\nu} R - N = C + S \quad (3)$$
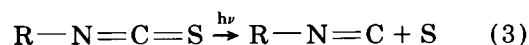
Such sulfur atoms are involved in the formation of the observed sulfide or multisulfide bonds as well as molecular sulfur S_8. The absence of the absorption band for the isonitrile groups ($2110-2160$ cm^{-1}) in the IR spectra of the polymer is indicative of isomerization of isonitrile to the more chemically stable nitrile groups:
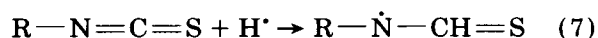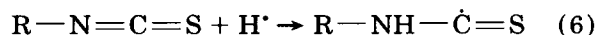
$$R - N = C \rightarrow R - C \equiv N \quad (4)$$
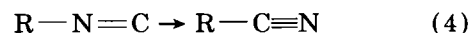
which have been detected in the structure of each investigated plasma polymer.

The abstraction of a hydrogen atom from the carbon atom in α-position with respect to the nitrile group leads to ketenimine bonding:

$$-CH_2 - C \equiv N \xrightarrow{e, h\nu} -CH = C = \overset{\cdot}{N} \xrightarrow{R^{\cdot}}$$
$$-CH = C = N - R \quad (5)$$
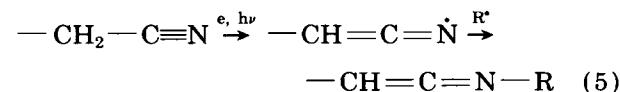
present in the PP–MITC, PP–PITC, and PP–AITC. It is noteworthy, that the lack of hydrogen at the α-carbon in aromatic nitriles prevents reaction (5) from occurring. This explains the absence of ketenimine groups in the PP–PHITC.

Another important reaction which may proceed in these plasmas is an addition of a hydrogen atom to the isothiocyanate group. Depending on the hydrocarbon substituent, attachment of a hydrogen atom may take place either on a nitrogen atom (for aliphatic substituent) or on a carbon atom (for aromatic substituent):[19]

$$R - N = C = S + H^{\cdot} \rightarrow R - NH - \overset{\cdot}{C} = S \quad (6)$$
$$R - N = C = S + H^{\cdot} \rightarrow R - \overset{\cdot}{N} - CH = S \quad (7)$$

Radicals resulting from reaction (6) may produce in the polymers a monosubstituted thioamide group,

whereas, radicals formed via reaction (7) may be involved in the production of N,N-disubstituted thioamide units. The differing reactivity of the radicals under consideration is reflected in the IR data. The absence of an absorption band from —NH— in monosubstituted thioamide groups (at 3100 cm^{-1}), was noted only in the case of PP–PHITC.

The hydrocarbon fragment of the monomer molecule may also undergo various plasma reactions. For example, the presence of olefinic linkages in PP–MITC and PP–PITC, and in their low molecular weight components, as shown by the IR and GC/MS, respectively, evidently accounts for plasma dehydrogenation reactions of aliphatic substituents in the monomer, and its resulting olefinization. Moreover, in the case of AITC even aromatization of the allyl group takes place, as proved by the presence of benzonitrile in the conversion products of this monomer (see compound 3 in Table II). The mechanism of these reactions seem to be very similar to those postulated for plasma conversion of the respective hydrocarbons.[21] Contribution of aromatic ring to the structure of most conversion products of PHITC (Table II) proves good resistance of this unit toward plasma fragmentation process and suggests its high content in the crosslinked polymer. However, some aliphatization of the phenyl ring also takes place, as revealed by compound 5 in Table II.

The active structures formed in the primary steps discussed above may subsequently undergo a number of secondary reactions producing low molecular weight and oligomeric products shown in Table II. The examples of these reactions have been presented for PHITC in our previous report.[2]

Finally, the present studies, which generally reveal the contents of the same structural units in the plasma polymer as in its low molecular weight fraction, allow one to conclude that these elementary reactions are not only involved in the oligomerization process but that they also can play a substantial role in the plasma polymerization process of the investigated organoisothiocyanates.

SUMMARY

The current work provides evidence for a high susceptibility of isothiocyanate group towards plasma fragmentation processes. The fragmentation pathway is dependent on the hydrocarbon fragments in the monomer molecule. In the case of alkane and alkene substituents (in MITC, PITC, and AITC, respectively) loss of the sulfur atom from the isothiocyanate group is the main reaction, whereas in the case of aromatic substituent (in PHITC), isomerization of this group to the thiocyanate unit, and subsequent dissociation to thiyl and nitryl radicals predominates.

Plasma reactions of isothiocyanate groups lead to the formation in the polymer of new structural units which were absent from the monomer. Depending on which heteroatoms are present in the monomer the new units may be of three types:

1. Nitrogen- and sulfur-containing units (thioamide and thiocyanate groups).
2. Nitrogen-containing units (nitrile, isonitrile, amidine, and in the case MITC, PITC, and AITC also ketenimine groups).
3. Sulfur-containing units (mono- and polysulfide, and thiocarbonyl groups, as well as molecular sulfur S_8).

Hydrocarbon groups in the monomers manifest different behavior in plasma. Aliphatic groups in the MITC and AITC undergo olefinization, whereas the aromatic substituent in PHITC reveals relatively strong resistance towards plasma fragmentation processes.

REFERENCES

1. G. Czeremuszkin, A. M. Wróbel, M. Kryszewski, *J. Appl. Polym. Sci.*, to appear.
2. G. Czeremuszkin, A. M. Wróbel, M. Kryszewski, *J. Polym. Sci. A Polym. Chem.*, **24**, 715 (1986).
3. G. Czeremuszkin, A. M. Wróbel, M. Kryszewski, *Proc. IUPAC 9th International Symposium on Plasma Chemistry*, Vol. 2, pp. 733–738.
4. A. M. Wróbel, M. R. Wertheimer, in *Plasma Deposition, Treatment, and Etching of Polymers*, R. d'Agostino, Ed., Academic Press, Boston, 1990, Chap. 3.
5. A. M. Wróbel, M. Kryszewski, and M. Gazicki, *J. Appl. Polym. Sci.*, **21**, 2013 (1977).
6. M. Gazicki, A. M. Wróbel, and M. Kryszewski, *J. Macromol. Sci., Chem.*, **A 20**, 583 (1983).
7. A. M. Wróbel, *Plasma Chem. Plasma Process.*, **7**, 429 (1987).
8. A. M. Wróbel, *J. Macromol. Sci., Chem.*, **A 26**, 743 (1989).

9. A. M. Wróbel et al., *Plasma Chem. Plasma Process.*, **10**, 277 (1990).

10. W. G. Deichert and M. C. Tobin, *J. Polym. Sci.*, **54**, S39 (1961).

11. N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964.

12. D. J. Curran and S. Siggia, in *The Chemistry of -CN Group*, Z. Rappoport, Ed., Interscience, London, 1970, Chap. 4.

13. L. Drobnica, P. Kristan, and J. Augustin, in *The Chemistry of Cyanates and Their Thio Derivatives*, S. Patai, Ed., Wiley, Chichester, 1977, Vol. 2, Chap. 22.

14. C. Wentrup, S. Fisher, A. Maquestiau, and R. Flamming, *J. Org. Chem.*, **51**, 1908 (1986).

15. E. Stenhagen, S. Abrahamson, and F. W. McLaferty, *Registry of Mass Spectral Data*, Wiley-Interscience, New York, 1974.

16. A. M. Kolchin, *Katalog Sokraschennych Mass-Spektrov*, Izdatelstvo Nauka, Nowosybirsk, 1981.

17. H. Yasuda, *Plasma Polymerization*, Academic Press, Orlando, 1985.

18. R. Jahn and U. Schmidt in *The Chemistry of Cyanates and Their Thio Derivatives*, S. Patai, Ed., Wiley, Chichester, 1977, pp. 343–355.

19. V. I. Trofimov and I. I. Chkheidze, *Khim. Vys. Energ.*, **5**, 404 (1971).

20. A. Fava, A. Illiceto, and S. Bresadola, *J. Am. Chem. Soc.*, **87**, 4791 (1965).

21. A. Fava, A. Illiceto, A. Cecon, and P. Koch, *J. Am. Chem. Soc.*, **87**, 4791 (1965).

22. H. Kobayashi, A. T. Bell, and M. Shen, *Macromolecules*, **7**, 277 (1974).