Plasma Polymerization of Organoisothiocyanates. I. Characterization of Deposition Process and Deposited Materials

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SYNOPSIS

Thin polymer films were produced from methyl-, n-propyl-, allyl-, and phenyl isothiocyanates in an RF plasma, induced in an electrodeless flow system. The deposition rate of polymer film as well as its composition was found to be dependent on the substrate position in the reactor tube. The distinct effect of the monomer structure and the monomer saturated vapor pressure on the polymer deposition rate suggest a molecular nature for the plasma polymerization process and an important role for adsorption in the deposition process, respectively. The surface free energy data, evaluated by contact angle measurements, reveal the polar character of the organoisothiocyanate plasma polymers. The polar component of the surface appears to increase with the sulfur concentration in the polymer film.

INTRODUCTION

While many different organic compounds have been used as the monomers in plasma polymerization little attention has been devoted to organosulfur compounds. The few literature reports which deal with plasma polymerized (PP) organosulfur materials reveal their many attractive properties. For example, PP–thiophene films may be used as high temperature resistant anticorrosive coatings for metals.[1] Thiophene and thiantrene plasma polymer films exhibited relatively high electrical conductivity;[2] the sulfur atoms, due to their electronic structure, appeared to be potentially capable of dominating the conduction mechanism. Thiantrene, thioacetamide, and 2,4-thiazolidone dione form plasma polymer films with relatively high photoconductivity.[3] Similar photoconductive behavior was also observed for PP–carbon disulfide films.[4] Thiophene plasma polymer films have recently been found to be a good material for passivation of GaAs surfaces in metal–insulator–semiconductor field effect transistors.[5,6] In our previous work[7] we focused attention on organoisothiocyanates, a new class of monomers for

plasma polymerization which are suitable for the production of films with useful electrical and photoelectrical properties due to the presence of the nitrogen and sulfur-containing substituent, $-N=C=S$.

The present study, being a continuation of our earlier work,[7] concerns plasma polymerization of methyl-, n-propyl-, allyl-, and phenyl isothiocyanates (MITC, PITC, AITC, and PHITC respectively). It is important to note that selected monomers are characterized by various S : N : C ratios and degrees of unsaturation, and these determine delocalization of π-electrons. In this paper we characterize a plasma deposition process for particular organoisothiocyanate monomers, the chemical composition of resulting polymer films, and their surface properties.

EXPERIMENTAL

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

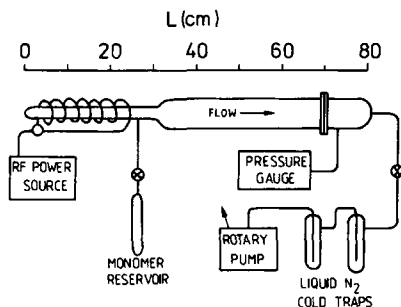Plasma polymerizations were carried out in a tubular (5 cm i.d.), electrodeless, inductively coupled

Figure 1 Schematic diagram of plasma reactor. L denotes the distance from the origin of the reactor.

plasma reactor shown in Figure 1. Polymer thin films were deposited on Corning 7059 glass pellets in an RF glow discharge operated at a frequency $f = 13.56$ MHz, output power $P = 100$ W, initial monomer vapor pressure (prior to the induction of plasma) $p_i = 6.7$ Pa, and flow rate $F \cong 4$ sccm. Pressure in the reactor was monitored using an MKS Baratron, Model 127A, pressure gauge. At these deposition parameters plasma was generated in the whole volume of the reactor. Thickness of the film was measured interferometrically. The elemental compositions of plasma polymers were determined by elemental analysis (EA).

Contact angle measurements were carried out at room temperature using doubly distilled water and methylene iodide (Loba-Chemie), according to the procedure described by Wróbel.[8] The polar and dispersive components of the surface free energy of polymer films were calculated using a model by Owens and Wend.[9]

RESULTS AND DISCUSSION

Polymer Film Deposition

It was found that all investigated monomers produce uniform films with thicknesses that range from hundreds of nanometers to several micrometers. Deposition rate curves, evaluated for each monomer, are presented in Figure 2. In the case of MITC, PITC, and AITC the deposition curves are linear over the whole interval of time examined, whereas for PHITC the linear shape of the deposition curve is observed after an initial 2-3 min of polymerization. A similar effect was observed previously[7] for polymerization of PHITC in a capacitatively coupled plasma reactor, and was related to the time needed to attain steady-state conditions in the system. However, variations of pressure in the reactor were
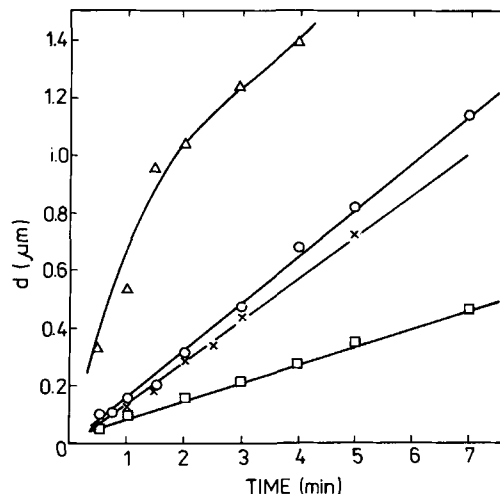

Figure 2 Time dependence of film thickness evaluated for plasma polymerized at $L = 45$ cm: ($\square$) MITC; (+) PITC; ($\bigcirc$) AITC; and ($\triangle$) PHITC.

noted during this time for all investigated monomers, as presented in Figure 3.

To elucidate the initial nonlinear character of the deposition rate curve noted for PHITC in Figure 2 we evaluated the effect of pressure variation in the reactor on the gas flow rate. Model calculations, carried out for the assumption of viscous and laminar gas flow in the reactor, showed that only in the case of PHITC did the observed pressure variation in the reactor cause substantial ($\sim 20\%$) increase of the monomer flow rate (F). In the case of the remaining three monomers, changes in F resulting from pressure variations were negligibly small ($< 1\%$). This effect may be attributed to much lower saturated vapor pressure for PHITC (25 Pa) as compared with the corresponding values for MITC, PITC, and AITC (2790, 400, and 413 Pa, respec-
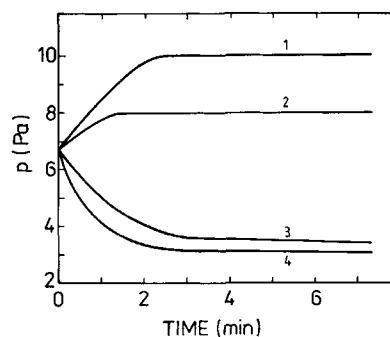

Figure 3 Pressure variation in plasma reactor during polymerization of (1) PITC, (2) MITC, (3) PHITC, and (4) AITC.

Table I   Parameter of Pressure Variation in Reactor p_g/p_i, Relative Monomer Vapor Pressure p_i/p_0, and Polymer Deposition Rate in a Function of Substrate Distance L from the Origin of the Reactor for Isothiocyanate Monomers

| | | | Deposition Rate, r [μm/min] | | |
Monomer	p_g/p_i	p_i/p_0	$L = 20$ cm	$L = 45$ cm	$L = 70$ cm
MITC	1.19	0.002	0.1	0.06	0.02
PITC	1.49	0.017	0.25	0.14	0.03
AITC	0.48	0.016	0.3	0.16	0.05
PHITC	0.49	0.268	0.5	0.20	0.12

p_i = pressure before plasma was induced; p_g = limiting total pressure during plasma was sustained; p_0 = monomer saturated vapor pressure at room temperature.

tively). According to the finding by Yasuda[10] and Sharma,[11] the deposition rate (r) of the polymer film in a low-temperature plasma increases with the value of P/FM (where P and M denote the discharge power and the molecular weight of the monomer, respectively). Therefore, it is reasonable to assume that the decrease in deposition rate during the initial stage of polymerization, observed only for PHITC (Fig. 2), may be related to the change of the monomer vapor flow rate.

Table I demonstrates the deposition rates (r) of the polymer films for various substrate positions in the reactor. The decrease of r with increasing substrate distance from the origin of the reactor (L), observed for each monomer, may be related to the drop in the concentration of polymerizable species along the reactor.

Pressure change in the reactor may be characterized by the p_g/p_i ratio, where p_g is the pressure of the gas under steady-state polymerization conditions and p_i is the initial monomer pressure. The values of this ratio evaluated from data in Figure 3 and listed in Table I provide information on the susceptibility of a particular monomer towards formation of nonpolymerizable gas which in the case

of hydrocarbons is mostly hydrogen.[12] Thus the value of $p_g/p_i > 1$ observed for MITC and PITC indicate that the evolution of hydrogen dominates in the fragmentation process of these monomers, whereas the value of $p_g/p_i < 1$ noted for AITC and PHITC proves that the monomers are mainly converted to polymerizable species. These results are consistent with the literature data[12] on the yield of hydrogen produced in plasmas of hydrocarbons with similar structures to those of the respective hydrocarbon substituents in the investigated organoisothiocyanates. Data in Table II indeed show substantially higher hydrogen yields for methane and propane with respect to those for propene and benzene.

Table II   Yield of Hydrogen Formed in Plasma Polymerization of Various Hydrocarbons[12]

Compound	Hydrogen Yield (y)
Methane	1.22
Propane	1.70
Propene	0.88
Benzene	0.11

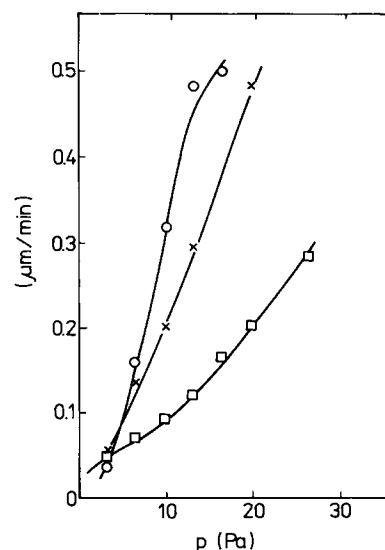$y = p_{H_2}/p_i$, where p_{H_2} is a partial pressure of hydrogen.

Figure 4 Deposition rate (r) of the polymer film as a function of the initial monomer pressure p_i evaluated at $L = 45$ cm for ($\square$) MITC, ($+$) PITC, and ($\bigcirc$) AITC.

The values of r for particular monomers, regardless of the substrate position in the reactor, remain in the relation: $r(\text{PHITC}) > r(\text{AITC}) > r(\text{PITC}) > r(\text{MITC})$. This suggests that the hydrocarbon substituent in the monomer molecule plays an important role in the polymerization process. Monomers containing the larger and unsaturated substituent (PHITC, AITC) reveal higher polymer deposition rates than those with smaller and saturated groups (PITC, MITC). This distinct effect of the monomer structure on r accounts for the molecular nature of the polymerization process which is also determined by the value of a composite parameter, P/FM. According to the finding by Sharma,[11] at values below a certain threshold value of this parameter $(P/FM < 10 \text{ GJ/kg})$ a plasma induced, molecular polymerization predominates, and the rate of polymer deposition strongly depends on the

structure of the monomer. At high P/FM values $(> 10 \text{ GJ/kg})$ the majority of monomers polymerize via an atomic polymerization mechanism and the structure of the monomer has very little influence on the rate of polymer deposition. The P/FM value for the present study, being approximately 0.1 GJ/kg, is lower than the mentioned threshold value by two orders of magnitude. This implies a molecular mechanism of plasma polymerization for the investigated monomers.

The molecular character of plasma polymerization also assumes a contribution of the adsorption process to the polymer deposition mechanism. This assumption was verified by correlation of r with the values of relative vapor pressure of the monomer p_i/p_0 (where p_0 is a monomer saturated vapor pressure at room temperature), which determines the adsorption of the monomer molecules on the surface
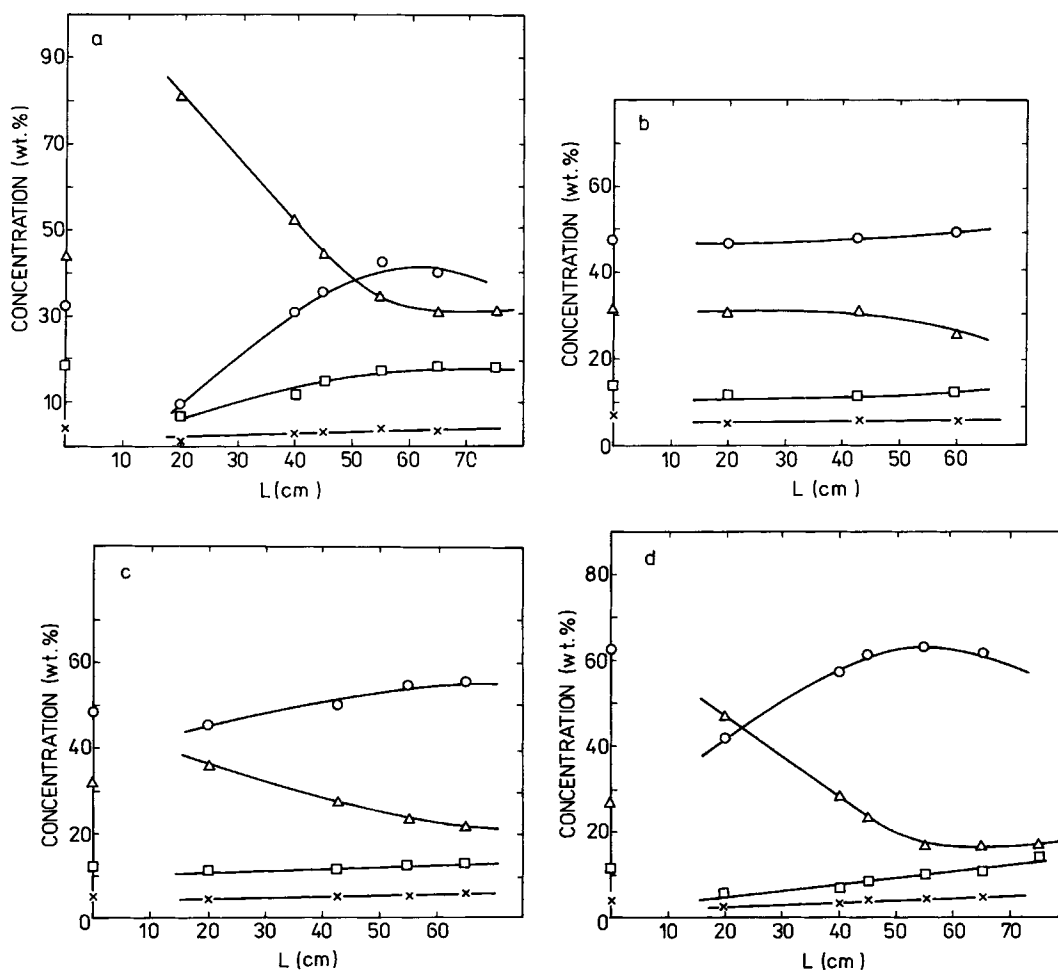

Figure 5 Elemental composition of polymer film deposited from: (A) MITC, (B) PITC, (C) AITC, and (D) PHITC, as a function of the substrate distance L from the origin of reactor: (O) carbon content; (△) sulfur content; (□) nitrogen content; (×) hydrogen content.

of substrate. The increase of r with increasing p_i/p_0 values, noted from the data in Table I, proves the validity of the aforementioned assumption. Moreover, this adsorptive character of the deposition process is also reflected by the curves of r versus pressure, presented in Figure 4, which appear to be very similar to the classical adsorption isotherms.[13] The effect of adsorption on the polymer deposition process has been reported for many other monomers [e.g. references 14, 15] and seems to be characteristic of plasma polymerization processes.

Elemental Composition of Polymer Films

Figures 5(a)-(d) present the elemental composition of PP-MITC, PP-PITC, PP-AITC, and PP-PHITC films, respectively, as a function of the substrate distance L from the origin of the reactor tube. The points marked at $L = 0$ correspond to the elemental composition of the monomers. In the case of PP-MITC and PP-PHITC [Fig. 5(a) and (d)] sulfur content decreases rapidly with the increase in L, while some increase of nitrogen content is noted. Similar behavior was observed previously[7] for PP-PHITC, produced in a capacitatively coupled plasma reactor. These results suggest a strong plasma fragmentation of $-N=C=S$ group and presumably independent contribution of nitrogen- and sulfur-containing fragments to the film formation process. In the case of PP-PITC and PP-AITC [Fig. 5(b) and (c)] the elemental composition does not vary significantly with increase in L and is comparable to that of the respective monomer. Thus it is reasonable to assume that the active species, incorporated to these polymers had partially different character and contained in their structure both, the sulfur and nitrogen atoms.

Thin films of investigated PP-isothiocyanates generally were found to be uniform, smooth, and amorphous, as shown by the electron microscopic observations and the results of X-ray as well as electron diffraction studies.

Elemental composition of the polymers deposited in the central part of the reactor, as well as composition of the monomers are presented in Table III. The oxygen contents in this table were assumed to be values complementary to 100%.

As it can be seen from Table III, the elemental composition of each polymer (except for oxygen content) is very similar to that of the respective monomer, although the oxygen contents were evaluated with much larger error than the remaining elements. The presence of this element is a general feature of plasma-polymerized materials and is attributed to a postplasma reactions of radicals or reactive groups in the polymer with the atmosphere.[16,17]

Surface Properties of Polymer Films

Surface properties of plasma polymer films were characterized by the evaluation of the surface free energy (γ_s) and its dispersive (γ_s^d) and polar (γ_s^p) components. For low values of the film thickness the surface energy of the film was found to vary with the thickness. This effect is exemplified in Figure 6 which shows the dispersive and polar components of the surface energy of PP-MITC film as a function of the deposition time. Although the dispersive component is nearly constant, the polar component is seen to increase with the deposition time, reaching a limiting value at $t = 5$ min which corresponds to the film thickness, $d = 0.3$ μm. The observed effect may be ascribed to the aforementioned change in

Table III   Elemental Composition of PP-organoisothiocyanates Deposited at $L = 45$ cm, and of the Monomers (in parentheses)

Plasma Polymer of	Elemental Composition (wt %)				
	S	N	C	H	O[a]
Methyl isothiocyanate	44.17	14.50	35.26	3.45	2.62
	(43.84)	(19.18)	(32.88)	(4.10)	—
n-Propyl isothiocyanate	30.82	10.39	47.43	5.94	5.42
	(31.68)	(13.86)	(47.53)	(6.93)	—
Allyl isothiocyanate	28.09	11.14	49.33	4.86	6.58
	(32.32)	(11.14)	(48.49)	(5.05)	—
Phenyl isothiocyanate	22.90	8.19	60.89	3.67	4.35
	(23.71)	(10.37)	(62.22)	(3.70)	—

[a] Oxygen content was assumed to be a value complementary to 100%.

the polymerization conditions at the beginning of the process (until steady-state conditions are reached), which presumably alters concentration of the polar groups in the surface structure of the film. Variation of the surface polarity with the film thickness (or deposition time) has also been observed for PP–hydrocarbon films.[18,19]

The surface free energy values of PP–organoisothiocyanates evaluated for the film thicknesses $d \geq 0.3$ μm, are shown in Table IV. As can be noted from these data, the monomers containing saturated hydrocarbon substituents (MITC and PITC) produce film of slightly lower γ_s^d and higher γ_s^p values than those of the films deposited from the monomers with unsaturated substituents (AITC and PHITC). The γ_s^d values may be considered in terms of our previous study[8] which proved that the dispersive component is very sensitive to the crosslinking in plasma polymers and increases with the degree of crosslinking. Therefore, some differences observed in γ_s^d values may arise from variation of the crosslink density in the surface structure of polymer films. The higher values of γ_s^d noted for AITC and PHITC are consistent with their aforementioned susceptibility towards crosslinking. The γ_s^p correlates well with sulfur content in polymer film and as can be seen from Tables III and IV, the polar component increases with the concentration of sulfur. Interestingly, the γ_s^p values presented in Table IV are generally much higher than those for PP–hydrocarbons,[8,20] being comparable (or in some cases even higher) to the polar component value for the plasma polymer of pyridine ($\gamma_s^p = 16.5$ mN/m).[8] In the light

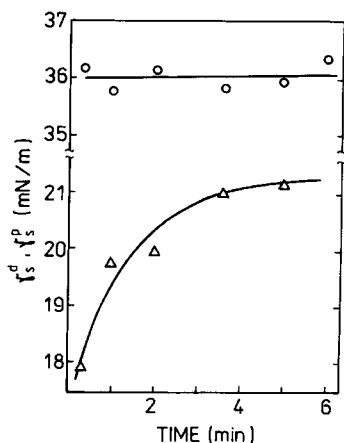**Table IV   Dispersive (γ_s^d) and Polar (γ_s^p) Components of the Surface Free Energy (γ_s) for Plasma Polymerized Isothiocyanate Films**

	Surface Energy, (mN/m)		
Plasma Polymer of	γ_s^d	γ_s^p	γ_s
Methyl isothiocyanate	35.8	21.2	57.0
Propyl isothiocyanate	37.6	17.2	54.8
Allyl isothiocyanate	39.2	13.8	53.0
Phenyl isothiocyanate	40.7	13.7	54.4

$\gamma_s = \gamma_s^p + \gamma_s^d$.

of these results PP–organoisothiocyanates may be categorized as materials of a rather strong polar nature.

Other interesting properties of these films as well as more detailed information on their chemical structure will be subjects of our future reports.

CONCLUSIONS

The main aspect of the present study may be summarized as follows:

1. The observed effect of monomer structure on the deposition rate of polymer film implies a molecular character of the plasma polymerization process.
2. Elemental compositions of organoisothiocyanate plasma polymers, deposited in a central part of the reactor at the plasma parameters used, are nearly similar to those of the respective monomers.
3. In the light of the surface free energy data, the organoisothiocyanate plasma polymers may be categorized as materials of polar character.

Figure 6 Components of the surface free energy of plasma polymerized methyl isothiocyanate film as a function of the deposition time: (O) Dispersive component (O) γ_s^d and polar component (△) γ_s^p

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