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Plasma Polymerized Chlorobenzene

^aA. GULDAN, ^bM. OMASTOVÁ, and ^aJ. HURAN

^a*Institute of Electrical Engineering, Slovak Academy of Sciences, SK-842 39 Bratislava*

^b*Polymer Institute, Slovak Academy of Sciences, SK-842 36 Bratislava*

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Polymer films using chlorobenzene as monomer were prepared by the method of plasma enhanced chemical vapour deposition (PECVD). IR absorption spectra of products of polymerization reaction were studied in the wavenumber range from 400 cm^{-1} to 4000 cm^{-1} . The spectra confirmed the presence of polymer product but on the other hand showed that plasma polymerization of chlorobenzene leads to the breaking of some bonds in the substituted benzene ring resulting in the appearance of conjugate alkenes of different lengths.

Polymer films are used extensively also in integrated circuit fabrication and in the fabrication of solid state sensing devices. Especially several kinds of hydrophilic polymers have been used as materials for humidity sensors [1–3]. One of the broad variety of potential monomers is chlorobenzene — an accessible organic halo compound.

Lot of methods are suitable for polymerization of this monomer. Chlorobenzene has been polymerized [4, 5] with aluminium chloride—cupric chloride to produce materials that consist mainly of poly(o-phenylene) structures with the chloride atom situated at the position 4 (Fig. 1). The product of polymerization reaction is red, with average degree of polymerization of 10–12. Chlorobenzene polymerized in a fairly low yield (from 6 to 14 %). Antimony pentafluoride converted chlorobenzene to low yields of polymeric species [6] presumably of polyphenyl-like structure.

Our attention has been directed to the method of plasma enhanced chemical vapour deposition.

Organic substance in the vapour phase being excited into luminescence by an electric discharge, a

solid film tends to deposit on all surfaces exposed to the luminous plasma. Depending on the conditions and the mechanisms of plasma polymerization the solid deposit from the plasma need not be formed in the conventional manner of functional groups uniting with each other in a repeating chain reaction. It is believed that ionic and ion-radical fragments are formed under the intense electron bombardment and recombine as they accumulate on the electrodes. The result is a complex intermolecular rearrangement of chemical bonds at more or less specific locations

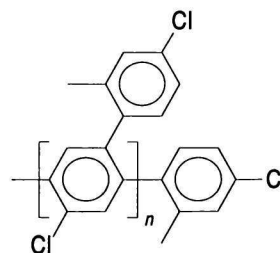


Fig. 1. Polymer structure of chlorobenzene.

in the monomer molecule, leading to a macromolecule of fairly well defined structure.

The present communication describes the experimental procedure for film preparation and presents data on film structure derived from the IR absorption spectra.

EXPERIMENTAL

Chlorobenzene, anal. grade (Lachema), was distilled under reduced pressure from calcium hydride before use.

The basic equipment for preparing polymer films consisted of an evacuated chamber with a source of chlorobenzene vapour and electrodes wired to an external RF (13.56 MHz) power supply. The flat aluminium electrodes were placed approximately 3–4 cm apart. The organic vapour was introduced through a capillary from an external liquid reservoir. Depending on the capillary diameter and temperature of the source it was possible to adjust the flow of chlorobenzene vapours to about $3.6 \text{ cm}^3 \text{ min}^{-1}$. The polymer films were deposited on silicon substrates at $\theta = 150^\circ \text{C}$, total reactor pressure being 90 Pa and power density 0.05 W cm^{-2} . The deposition rate of polymer films under these conditions was 40 nm min^{-1} . A monocrystalline silicon substrate (Tesla Rožnov) with polished surface was used. The rate of deposition of polymer film was determined by a crystal controlled with the help of speed indicator of growth of thin layers. The thickness of the prepared polymer layers was determined by interference microscope.

RESULTS AND DISCUSSION

The films prepared by plasma polymerization of chlorobenzene are of good mechanical properties. Under mechanical impact they do not rub off, nor do they peel off after substrate breaking.

The films for IR absorption spectra measurements were between 300 nm and 400 nm thick. Fig. 2 shows a typical differential absorption IR spectrum of the prepared films in the wavenumber range from 400 cm^{-1} to 4000 cm^{-1} . The absorption bands in the range of $\tilde{\nu} = 3000\text{--}3070 \text{ cm}^{-1}$ correspond to the stretching vibrations of C—H groups of the monosubstituted benzene derivative [7]. Relatively strong absorption peaks at 2867 cm^{-1} and 2926 cm^{-1} , respectively are attributed to C—H stretching vibrations in conjugated alkenes. Their presence in the IR spectrum is probably connected with the opening of rings of some chlorobenzene molecules leading to the creation of conjugated alkenes of different lengths due to plasma affection. Further vibration peaks of alkenes appear at the wavelengths $1600\text{--}1700 \text{ cm}^{-1}$ and $1300\text{--}1400 \text{ cm}^{-1}$ and they are probably superimposed by vibrations of particular bonds in chlorobenzene molecules. Absorption bands between 1600 cm^{-1} and 2000 cm^{-1} are attributed to off-plane deformation vibrations of hydrogen atoms in the phenyl groups, manifested in this range by combination and harmonic frequencies. In the wavenumber range $750\text{--}1600 \text{ cm}^{-1}$ there are also absorption peaks accounting for vibrations of C—C bonds in the benzene rings. In the range $1320\text{--}1580 \text{ cm}^{-1}$ appear peaks accounted to the stretching mode vi-

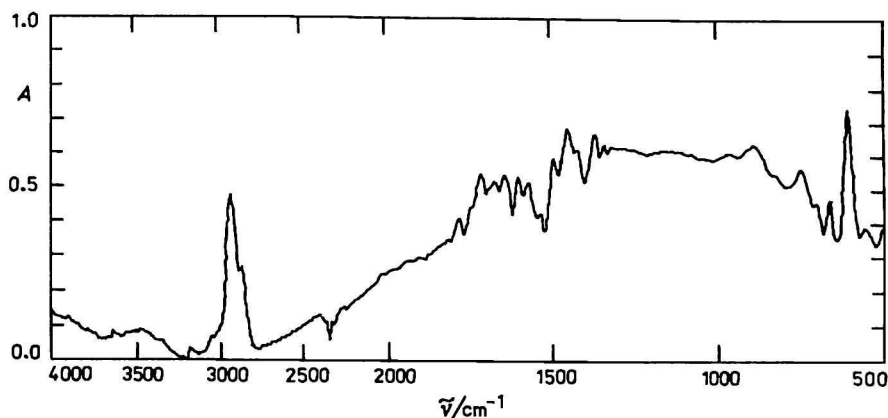


Fig. 2. IR spectrum of plasma polymerized chlorobenzene.

The measurements of IR absorption spectra of polymerized chlorobenzene films were carried out using Perkin—Elmer G 983 apparatus. The spectrum can be considered differential, that is the spectrum of polymerized chlorobenzene on substrate obtained by measurement was subtracted from the spectrum of pure silicon substrate.

brations of C—C bonds in the benzene ring. At the wavelengths $1025\text{--}1271 \text{ cm}^{-1}$ we may find absorption bands corresponding to the plane deformation vibrations of C—H groups. Typical wavelengths of absorption maxima belonging to the vibrations of C—Cl groups in chlorobenzene molecules are 703 cm^{-1} and 1085 cm^{-1} , respectively [8].

Information concerning the structure of the polymer was provided by IR spectrum in the region from 700 cm^{-1} to 900 cm^{-1} . The 1,2,4 substitution in the polymer structure (Fig. 1) was indicated by absorption maxima at $\tilde{\nu} = 894\text{ cm}^{-1}$ for isolated hydrogen ($860\text{--}900\text{ cm}^{-1}$ [9]) and 825 cm^{-1} for two adjacent hydrogens ($800\text{--}860\text{ cm}^{-1}$ [9]). A band at $\tilde{\nu} = 750\text{ cm}^{-1}$ can be assigned either to three adjacent hydrogens at one end of the chain arising from the initiation or to four adjacent hydrogens arising from termination by the *ortho* attack to halogen for four adjacent hydrogens [9].

Using plasma polymerization of chlorobenzene it is possible to get smooth defect-free and water-insoluble polymer films with perfect adhesion to silicon. The colour of the poly(chlorobenzene) thin films on silicon substrates depends on interference effects. The characteristic colour depends on the film thickness, its index of refraction and the spectral distribution of the viewing light. It is correct to state that plasma polymerization leads to the breaking of some bonds in the substituted benzene ring resulting in the appearance of conjugated alkenes of different lengths. However, the structure shown in Fig. 1 arose by plasma polymerization of chlorobenzene, which is confirmed by IR spectra.

The prepared polymer films are soluble in chloroform or benzene only after several hours of conditioning by solvent under increased temperature.

Osmometrically determined molecular mass of the product allows to state an average degree of polymerization of 7–9.

Plasma polymerized chlorobenzene films could be used as humidity sensitive layers. A detailed study of the response properties of the prepared polymer films due to moisture sorption is in progress.

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