Deposition of Poly-*p*-xylylene Films by Plasma Decomposition of Cyclodi-*p*-xylylene

INTRODUCTION

Poly-*p*-xylylene (PPX) films and coatings have usually been prepared by the Gorham method.[1] The method is based on pyrolytic decomposition of the cyclic dimer, di-*p*-xylylene (DPX), to the active *p*-xylylene (PX) monomer on a hot wall (about 870 K) under low pressure (between 10 and 100 Pa). PX generated in the pyrolytic reactor passes through the cooling zone to the deposition chamber, condenses, and polymerizes on surfaces at a temperature of about 300 K or lower.

However, pyrolysis is not the only possible method of decomposition of multiatomic molecules in the gaseous state. It is well known that this process also takes place in glow-discharge plasma. The aim of the work described here was to study the possibility of PPX film deposition by plasma decomposition of DPX at the stage of monomer generation.

EXPERIMENTAL

The experiments were carried out in a deposition system like the pyrolytic one, described in detail elsewhere,[2,3] in which the pyrolytic reactor with the cooler was replaced by a hot-walled plasma reactor.[4] The reactor wall temperature was reduced from 870 to 420–440 K. Plasma was excited in pure DPX vapor or in DPX diluted in argon or nitrogen. An rf generator (5.28 or 40.68 MHz) was capacitively coupled with the reactor by a matching network. The power introduced in the plasma did not exceed 30 W. The deposition rate and the film thickness were measured by a quartz microbalance. IR absorption spectra were taken using a UR-20 spectrometer (Carl Zeiss, Germany). Thermoanalyses were performed on an OD-102 derivatograph (MOM, Hungary). The DPX sublimation rate was between 0.3 and 1.5 mg/s; the PPX deposition rate between 3 and 8 nm/s.

RESULTS AND DISCUSSION

The IR spectra of "plasma" and "pyrolytic" films are represented in Figure 1. The comparative analysis of these spectra revealed no apparent differences between them. There were also no significant differences between IR spectra of "plasma" PPX deposited from pure DPX vapor and those from DPX diluted in argon or nitrogen.

The comparative thermal analysis of "plasma" and "pyrolytic" PPXs demonstrated their qualitative resemblance with some differences in individual temperature ranges. The thermogravimetric diagram (Fig. 2) shows the mass increased due to thermal oxidation in the 450–550 K range for the "pyrolytic" sample. The "plasma" sample showed no mass variations due to thermal oxidation over this range. There are also some features within the 580–750 K range. It should be noted that the "plasma" sample also has differences in the DTA diagrams. (It is well known that "pyrolytic" samples produced at different deposition conditions can also have different DTA diagrams.) The origin of these differences was not established at this stage of investigation.

The main mechanical properties of the "plasma" films depend on the process conditions and lie within the bounds of variation for the "pyrolytic" films.[5] For example, the typical mechanical characteristics of the "plasma" films formed at the most simple process conditions are tensile strength of 40 MPa, tensile modulus of 1.8–2.2 GPa, and elongation at break of 20–50%. Resemblance of IR spectra, mechanical properties, and the other characteristics (appearance, adhesion to different substrates, ability to form coatings on the surfaces of narrow clearances, and so on) of two types of PPX confirms their qualitative identity.

CONCLUSIONS

Based on the above facts, it is concluded that plasma can be used for the PPX film deposition, and this method has been patented.[6] One should notice that the polymer produced by the proposed method differs from polymers synthesized from volatile organic compounds in glow discharge plasma.[4] The former polymer consists of linear chain molecules of a regular chemical structure (like usual linear polymer); meanwhile, the latter ones have cross-linked irregular molecular structures and possess special properties. PX resulting from plasma decomposition of

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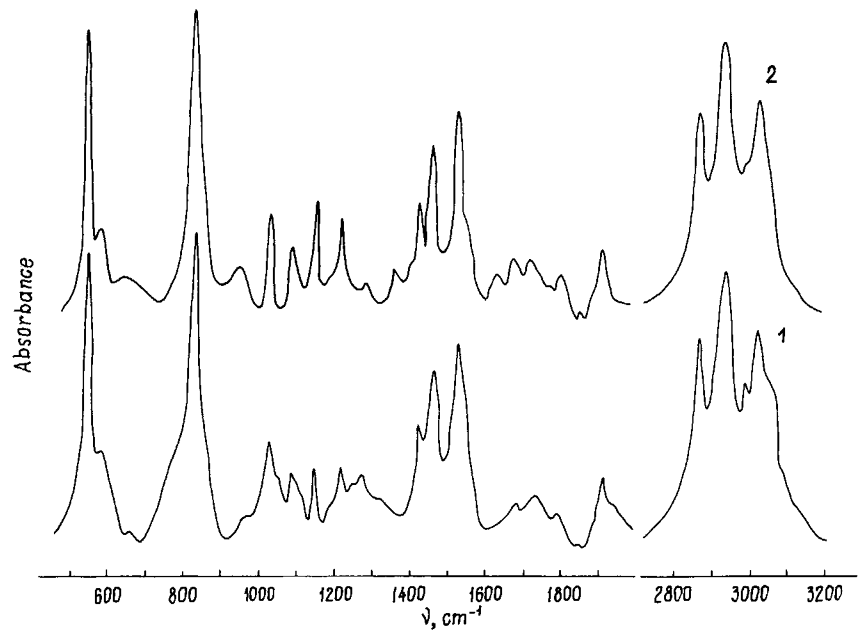

Figure 1 IR spectra of (1) "plasma" and (2) "pyrolytic" PPX films.

DPX is capable of transportation to considerable distances from the zone of generation. The products of plasma decomposition of other organic compounds form deposits located on the surfaces that are in contact with the plasma or just found following the plasma zone. The method proposed has some advantages compared with the "pyrolytic" one:

- Low temperature of the plasma reactor.
- Small dimensions of the decomposition zone due to high efficiency and volume character of electron activation of the monomer molecules.
- Great possibilities for modifying the film properties by varying the gas mixture composition and rf power.
- Possibilities for fast changing the thermal conditions of the processes due to the low temperature of the reactor and simplicity of converting the rf power into heat.

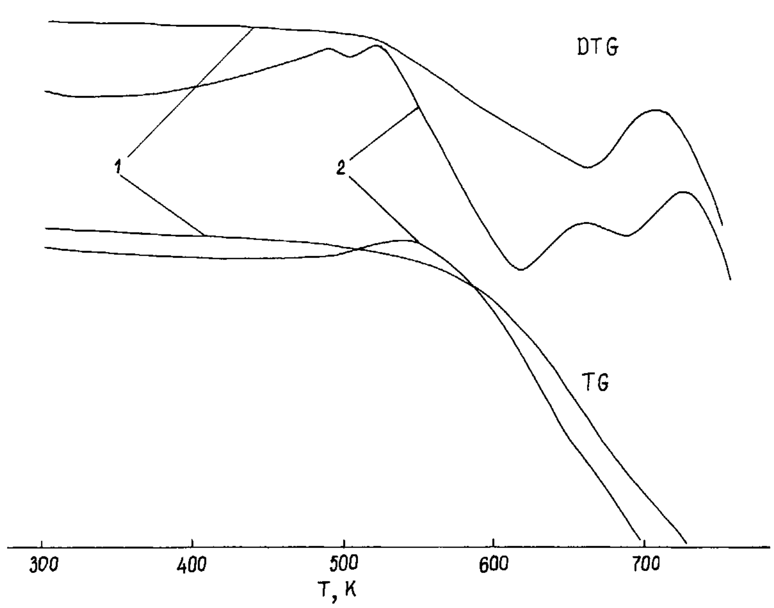

Figure 2 Thermogravimetric diagrams of (1) "plasma" and (2) "pyrolytic" PPX films.

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