DENSE MEDIUM PLASMA REACTION: A NEW APPROACH TO PLASMA CHEMISTRY

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Benzene reacted under dense medium plasma (DMP) conditions (liquid phase; 20°C; DC discharge) resulted in a solid phase insoluble poly-yne-polyacetylene type structure and in a benzene soluble complex mixture of aromatic hydrocarbon having unsaturated side chains. The solid phase polymer has a poly-free-radical nature and exhibited superior thermal stability. Potential applications of DMP technique for reacting a wide range of materials and/or their mixtures are discussed.

Introduction The electrical discharge method for creating the cold plasma state has two main disadvantages: only low quantities of materials can be processed and the processing must generally be under low pressure conditions [1-4]. In this paper a new approach to plasma chemistry is described and involves ignition of argon-electrical-discharge in caloric energy controlled, condensed (liquid-phase) media. The dense medium plasma (DMP) induced reactions of benzene are analyzed, and the potential for development of a new plasma chemistry is discussed.

Experimental A schematic diagram of DMP reactor and a sketch of the plasma installation are presented in Figure 1. The DMP reactor is a Pyrex glass, tubular shaped (Length-150 mm; ID-60 mm), double-walled (Pyrex glass jacket, 12, for thermostating purposes) reaction vessel (13), provided with removable top (2) and bottom (9) caps. The caps are tightly fastened to the reactor by means of silicon rubber 0-rings (15). The electrical discharge is sustained between the two vertically positioned electrodes. Both electrodes have a hollow-cylindrical form, with smooth disc-shapes and triangular vertical-plane cross sections. The upper electrode is connected through an elastic coupling to a rotating system, which allows the controlled rotation of upper electrode between the limits of 0-5,000 rpm.

Symmetrically positioned (120 degrees) three holes (3), located at the middle range of the electrode, and the axial inner channel (4), assure by centrifugal force, intense recirculation of the reaction media. The lower electrode (9) has a fixed position during the discharge, however it can be vertically translated by means of a metric thread system (17) for selection of the desired distance between the electrodes. The inner channel (10) permits, at the same time, the feeding of inert or reactive gases before and during the plasma reaction, both for reaction medium degassing processes and for synthetic purposes. In and out thermostat connections (6 and 14) permit the recirculation of cooling agents, such as thermostatically-cooled alcohol or liquid nitrogen. Teflon-tubing connections (ID-5mm) (5), mediate the centrifugal-force driven recirculation of reaction media from the bottom to the top of the reactor. Stainless steel tubing (ID-5mm), (7) and (16), assure the removal of final reaction products and the elimination gaseous components.

The experimental conditions employed during the DMP reaction (e.g. for benzene) were as follows: starting medium: benzene; volume of benzene: 250 ml; inert gas: argon; spacing between the electrodes: 0.5 mm; angular speed of upper electrode: 5,000 rpm; cooling-agent temperature: 10^{o}C; DC voltage at the beginning of the reaction: 800 V; DC voltage during plasma reaction: 30-40 V; DC current during reaction: 3-4 A; reaction time: 30 minutes; nature of electrodes: stainless steel, cooper and graphite.

Results and Discussions The comparative IR spectra of the solid phase black polymers produced with stainless steel (SP), cooper (CP) and graphite (GP) electrodes in the DMP reactor are presented in Figure 2. One can notice an almost total absence of the absorption in the range of 2850-3000 cm^{-1}, associated with C-H symmetric and antisymmetric stretching vibrations. Vibrational frequencies characteristic of aromatic groups (3000-3100 cm^{-1} and 690-780 cm^{-1}) are also absent in the spectra. These findings strongly suggest intense dehydrogenation and aromatic ring opening processes. The existence of a strong absorption at 1639 cm^{-1} indicates the presence of considerable unsaturation (-C=C- bonds). High resolution IR data collected in the 1500-1700 cm^{-1} range emphasize also the existence of unsaturation in all compounds, regardless of the composition of the electrodes. The presence of a relatively intense (broad) absorption around 3454 cm^{-1} suggests the development of post-plasma moisture absorption processes.

ESCA and elemental analysis data are in good agreement with the FT-IR results, indicating a high carbon content for all samples. A lower carbon content (81 %) and a higher oxygen content (16%) can be noticed in the case of the SP polymer

in comparison to the CP one (C=95.7% and O=4.31%). Metal contamination was evidenced by ESCA only in the case of the SP formed structure (Fe=1.67 %). Elemental analysis data indicate a significantly low hydrogen content for both samples.

High resolution (HR) MS spectra of the SP, CP and GP polymers (temperature of solid probe holder: 400 ^{0}C) show that even the volatile fractions have relatively high molecular weights (m/z > 800) and that the electron induced fragmentation results essentially in m/z= 26 (-CH=CH-), 25 (-CH=C-) and 24 (-C≡C-) units, and their higher homologs. Plasma induced ring opening mechanisms, accompanied by dehydrogenation processes is suggested to be responsible for the formation of these structures. These reactions could lead also to stable poly-free-radical polymeric systems with unusual magnetic properties.

The thermal behavior of the black DMP polymers was investigated with TG/DTA. All samples showed a strong exothermic event in the interval of 150-600 ^{0}C; this phenomenon can be explained by molecular reorganization and decomposition processes. The weight loss patterns are however significantly different. The GP polymer is the most thermally stable structure with a weight loss of only 0.8 % at 443^{0}C and 21.3 % at 600 ^{0}C while the SP and CP samples show 9 and 24 % (443 ^{0}C) and 28 and 49% (600 ^{0}C) weight loss, respectively. The initiation of thermal degradation reactions also differs for the three samples. The highest thermal degradation initiation temperature is noticed for the GP polymer (400 ^{0}C).

The free radical nature of the polymers was investigated by ESR. Figures 3 and 4 show the DPPH (standard) and the CP ESR spectra recorded at room temperature. A symmetrical signal is observed in both of the cases. Spectra recorded at low temperatures (-123^{0}K) presented a similar pattern. It is noteworthy that the spectra of the SP and GP polymers could not be recorded because of the difficulties in balancing the instrument.

The SP and GP polymers exhibit ferromagnetic properties (the powders of these materials can be translated with a permanent magnet). This behavior can be explained by metal contamination or by the existence of stable biradicals in the structure of the polymers.

Scanning electron microscopy provides information on the surface morphology of the polymers. The images (x 20.000) show the presence of clustered spherical and lamelar type structures (Fig. 5 a and b).

FT-IR, NMR and GC-MS data collected for the benzene soluble fractions indicated the existence of very complex molecular mixtures composed of aromatic structures bearing unsaturated sidechains. The structures of some of the compounds identified are presented in Figure 6. The presence in the mixtures of higher molecular weight saturated hydrocarbon-chain attached aromatic structures is also suggested.

Conclusions DMP is a new type of discharge initiated in condensed phase media (liquids, liquid mixtures, solutions, and dispersions). The method permits the processing of large quantities of materials in inert or active gas environments, under controlled temperature conditions. Analytical data indicate that the polymers, originating from benzene, are built-up of -CH=CH-, -CH=C- and -C≡C- units; they are thermally stable and exhibit a poly-free-radical nature. The SP and GP polymers exhibited ferromagnetic properties. This behavior might be explained by metal contamination or by the incorporation of stable biradicals (triplet state) into the polymeric structures. This finding opens up possibilities for creating metal particle dispersed composite polymeric materials. Electron microscopy data indicate that the black polymers have an ordered nature.

The benzene soluble fractions (LSP, LCP and LGP) were mainly composed of aromatic structures (different than benzene) bearing unsaturated side groups. The analytical data derived from both the insoluble and soluble fractions indicate the presence of a ring opening and molecular reorganization mechanism, associated with dehydrogenation processes, under DMP conditions. Clearly this new plasma chemistry is complex but holds great potential for future development of valuable novel materials.

REFERENCES

1. R. d'Agostino, ed., Plasma Deposition, Treatment and Etching of Polymers, Academic Press, N.Y. (1991).
2. M.Shen and A.T. Bell, Plasma Polymerization, ACS Symposium Series, 108 (1979).
3. H. Yasuda, Plasma Polymerization, Academic Press, N.Y. (1985).
4. H.V. Boenig, Plasma Science and Technology, Ithaca, N.Y. Cornell University Press (1982).

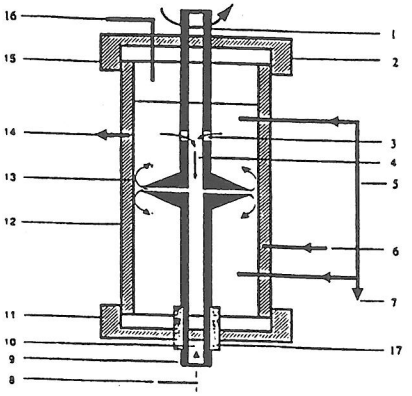

Fig.1 Schematic diagram of DMP reactor

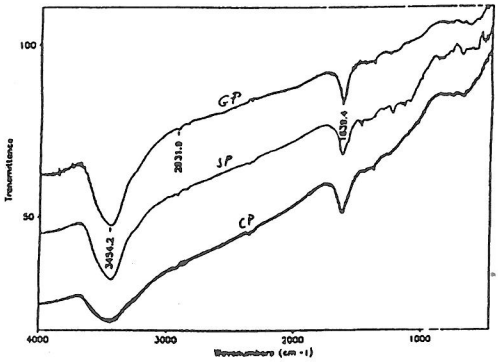

Fig.2 Comparative IR spectra of SP, CP and GP

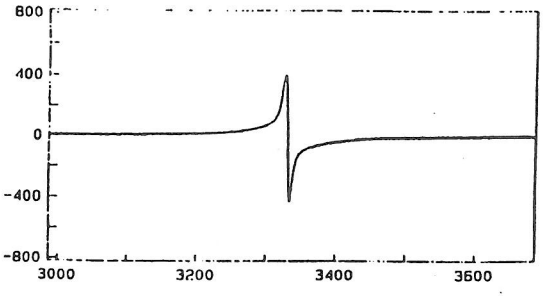

Fig.3 ESR spectrum of DPPH

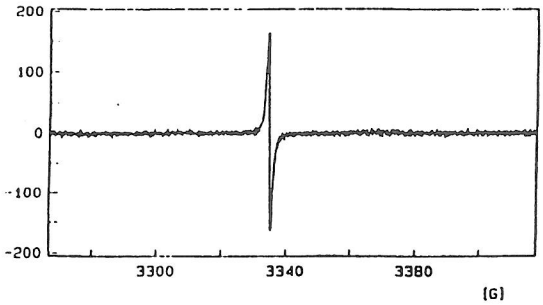

Fig.4 ESR spectrum of CP (at room temperature)

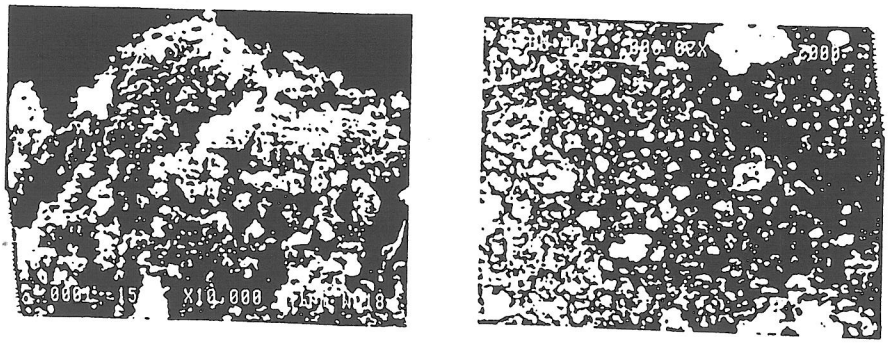

Fig.5a SEM image of clustered spherical structures
of SP (x10,000, left, x20,000, right)

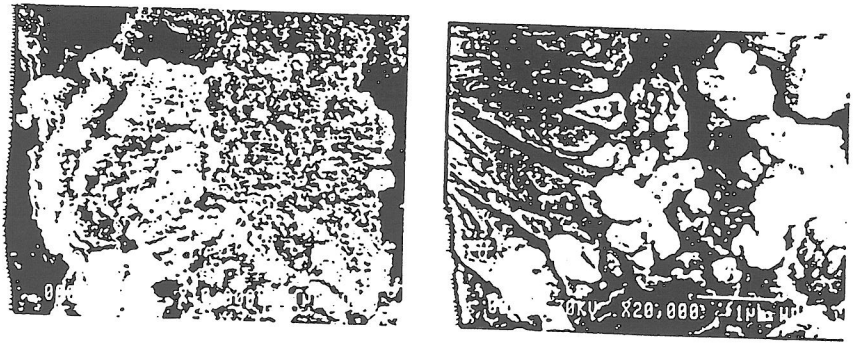

Fig.5b SEM image of clustered lamella structures
of CP (x10,000, left, x20,000, right)