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SHORT COMMUNICATIONS

Thin Films Plasma Polymerized from Propylene Oxide and Carbon Dioxide Mixture

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Considerable attention has been paid to plasma deposited films which can be used as a permeable membrane,[1,2] a biomedical material,[3] and a gas sensor device.[4] It is well-known in this field that the structure and properties of the plasma polymers are altered by the incorporation of heteroatoms such as oxygen,[5] nitrogen,[1,6] sulfur,[2] and iodine.[7] Such thin film prepared from nitrogen-containing monomer, for instance, exhibits hydrophilicity.

On the other hand, interest has been shown in an attempt to transform CO_2 into polymeric materials from the viewpoint of fixation of CO_2. High polymers using CO_2 as a direct starting material have been made in the copolymerization of CO_2 and epoxide in the presence of diethylzinc and co-catalyst.[8] CO_2 was also copolymerized with vinylether[9] and butadiene[10] in this way, and few thin films from plasma copolymerization of a monomer and CO_2 have also been prepared. During work on a totally artificial biomembrane model,[11-13] our effeort was directed toward plasma deposited film in order to obtain a novel permeable membrane with hydrophilicity.[5,14,15]

In this communication, we report the plasma polymerization of PO in the presence of CO_2.

EXPERIMENTAL

The monomer, propylene oxide (PO), was purified by distillation and used after degassing by a few cycles of the freeze-thaw method. Carbon dioxide (99.95%, containing as impurities 0.05% of water) and argon (99.99%) were obtained from Taiyo Sanso Co. The plasma reactor was fabricated from a glass chamber (separable flask: 11 cm height × 8 cm diameter) and copper plate electrodes, the one surrounded the reactor (hot electrode: 5 cm width × 50.24 cm long) and the other placed under the reactor (ground electrode: 20 cm × 25 cm), as shown in Figure 1. The rf power

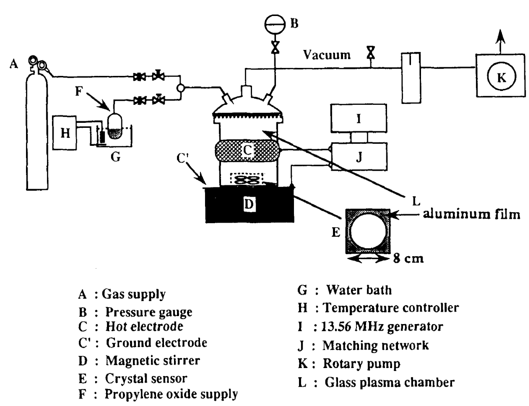

Figure 1. Schematic illustration of the plasma reactor.

generator (Nippon Denpa Kogyo NFG-150) was operated at a fixed frequency of 13.56 MHz and had a maximum power out let of 150 W. CO_2 or Ar from cylinder and PO vapor from the flask (F in Figure 1) can be fed through feed lines. The feed lines are constructed mostly of stainless steel tubes, 0.25 inch (6.4 mm) o.d. and Swagelok fittings. The system pressure was controlled by feeding gases and PO flow rate by adjusting a metring valve. The flow rates were determined by measuring system pressure increase over a given time interval by Baratoron absolute pressure gauge (MKS), then converted to flow rate (sccm). In these experiments, flow ratios of CO_2 to PO and Ar to PO were maintained 0.5 to 0.7 and 0.4 to 0.7 respectively, unless otherwise specified. System pressures before plasma initiation were at equilibrium of 700 mTorr in all cases. The deposition rate of plasma polymer (R_d) was calculated from the thickness of the thin film deposited on a crystal sensor placed on the bottom of the plasma chamber, using a JOEL Model TM200R. IR measurements were carried out with a JASCO IR 810 spectrometer. The surface of the thin films obtained were analyzed by ESCA using a Simadzu ESCA 750.

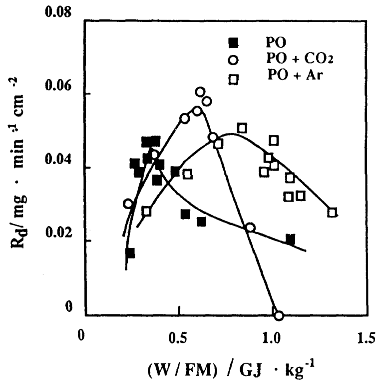

Figure 2. Relationships between polymerization rate (R_d) and W/FM in the plasma polymerization of PO, PO + CO_2, and PO + Ar system: flow ratio of $CO_2 = 0.71$; flow ratio of Ar = 0.57.

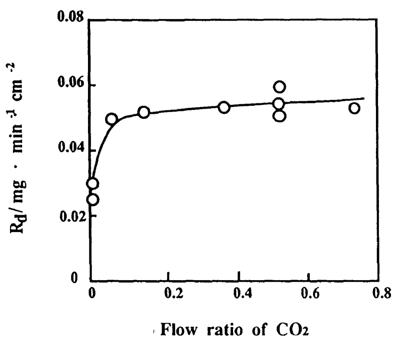

Figure 3. Relationship between polymerization rate (R_d) and flow ratio of CO_2 in the plasma polymerization of various PO + CO_2 systems within power range of 0.56—0.64 $GJ \cdot kg^{-1}$.

RESULTS AND DISCUSSION

Figure 2 shows the effect of plasma energy density (W/FM) on R_d for the plasma polymerization of PO, PO + CO_2, and PO + Ar systems with different input power level ranging from 20 to 80 W. W/FM, expressed in Joule per mass of gasses,[16] represents the energy input per unit mass of fed gas molecules, where W, F, and M represent input power (W), mass flow rate (sccm), and molecular weight, respectively.

In the mixed gaseous system, the molecular weight used was the average of that of each molecules. R_d showed convex curves against W/FM in all cases. Comparing the maximum R_d obtained from the top of convex curves, the PO + CO_2 system exhibited the highest among three systems, and appeared in the order of PO, PO + CO_2 and PO + Ar system against W/FM. These results suggest that CO_2 molecules are possibly incorporated into polymer as C=O and C–O–C groups, and CO_2 as well as Ar behave as an energy absorbent in these mixed gaseous systems. The plasma polymerization of PO + CO_2 system was also carried out within W/FM range 0.56—0.64 $GJ \cdot kg^{-1}$, varying the CO_2 flow ratio from 0 to 0.71 and adjusting the pressure before plasma initiation at equilibrium of 700 mTorr. From the relationship between the R_d and CO_2 flow ratio as shown in Figure 3, it is suggested

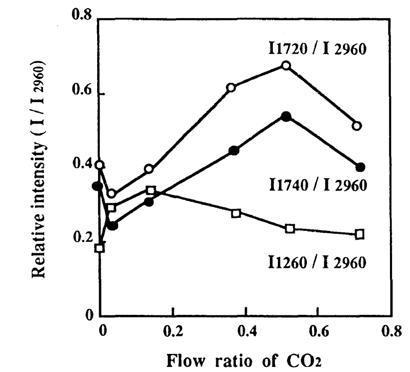

Figure 4. Relationships between relative intensity in IR (I/I_{2960}) and flow ratio of CO_2.

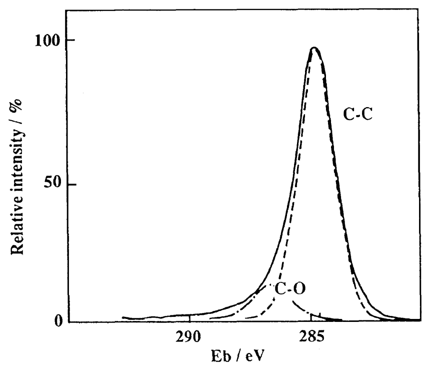

Figure 5. ESCA spectrum of polymer obtained from plasma polymerization of PO systems.

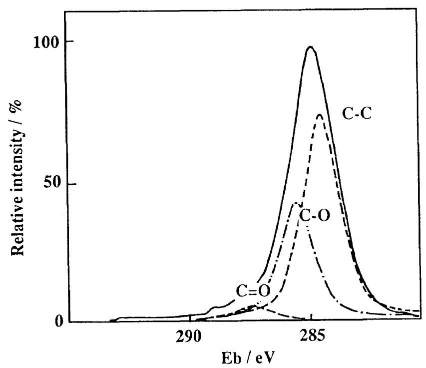

Figure 6. ESCA spectrum of polymer obtained from plasma polymerization of PO + CO_2 systems (flow ratio of $CO_2 = 0.51$).

that CO_2 plasma causes no decrease in R_d and CO_2 molecules incorporate into the polymer as a comonomer since R_d gradually increases with increasing CO_2 content in this condition. In order to confirm the incorporation of CO_2 in the thin film, the samples were studied by IR and ESCA. Figure 4 shows the relative intensities of 1720 and 1740 cm^{-1} based on C=O stretching and 1260 cm^{-1} based on C–O–C stretching against 2960 cm^{-1} based on CH_2 stretching in IR spectra for samples prepared by varying the CO_2 flow ratio from 0 to 0.71. The relative intensity of C=O increases with increasing ratio of CO_2 in feed. Figures 5 and 6 represent the ESCA results of PO plasma polymers prepared at a 0.51 CO_2 flow ratio and without CO_2, respectively. It was found in comparison between these two ESCA spectra that besides C–C bond a peak based on C–O is detected in plasma polymer prepared without CO_2, whereas there exist two rather strong peaks probably based on C–O and C=O bonds in the case of the CO_2 + PO system. From the results of the preparation and characterization of the plasma polymerized PO thin film obtained here, it is concluded that CO_2 can be transformed into polymeric material by plasma polymerization. Specific gravity (d^{25}) was measured as one of the physical properties of the thin films. d^{25} of samples were found to be 1.08—1.18 g·cm^{-3} by the floating method using a mixed solvent of *m*-xylene and carbon tetrachloride at 25°C. The permeation characteristics of the thin films obtained here will be described elsewhere.

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