



TECHNICAL CORNER

UROD Bulletin
Report Jan 1963

COX BG63 0713

NEW MATERIALS FROM HIGH TEMPERATURE AND HIGH PRESSURE PROCESSES

Transformations in materials occurring as the result of high temperature and high pressure reactions are intimately related to the performance of military materiel, and studies of the transitory and final effects produced under these conditions should lead to materials with useful new properties. Recent research has demonstrated that high pressures can have a decided effect on the rates of chemical reactions which proceed through ionic transition states. Little is known of constitutional diagrams in which pressure is a parameter, because of experimental difficulties on obtaining data on phase boundaries, solubilities, etc., at high pressure. Studies in this area will provide basic information useful in the production and performance of military materiel. This report summarizes information obtained to date in this AROD-supported Military Theme.

I. NEW APPARATUS

Tetrahedral Ram

A tetrahedral anvil high pressure apparatus has been constructed, with modifications and adaptations to allow *X-ray diffractometry analysis* of samples subjected to pressures up to 98,000 atm. The X-ray tube is mounted in a cylindrical cross-axis hole in one of the hydraulic rams. The tetrahedral sample chamber is made of solid LiI to reduce X-ray absorption, and is formed by pressing polycrystalline LiI in a suitable die. The system has been tested by measuring X-ray diffraction patterns from KCl at various pressures; the KCl volume transition reported by Bridgman at approximately 20,000 atm. has been observed.¹

II. INORGANIC REACTIONS AND MATERIALS

1. Aluminum Oxide

Application of pressure induces *thermoluminescence* in γ -irradiated Al_2O_3 single crystals, indicating geological age-dating by measuring thermoluminescence should take *pressure effects* into consideration.⁵

2. Boron

A non-equilibrium *transformation boundary* between α and β rhombohedral boron has been determined between 20,000 - 40,000 atm.

3. Boron-Phosphorus System

Three new *high temperature phases* have been detected in addition to cubic BP and hexagonal $B_{13}P_2$; a fcc phase with lattice constants of 5.71-5.76A, and two primitive cubic phases with lattice constants of 5.53 and 5.70A.⁴

4. Carbon

Graphite produced from diamonds at 40,000 atm. and 2,000°C contains some rhombohedral graphite. Only the hexagonal form has been found at room temperature; thus, rhombohedral graphite may be an *intermediary* in diamond formation.⁴

5. Carbon Disulfide

Polymer has been obtained at 15,000 atm., 20°C, and γ dose rate of 18Mr/hr.⁶ Gradual increase in G-value for conversion of monomer to polymer noted with increasing temperature and pressure. Most samples are intensely black solids which swell in but are not dissolved by the monomer. Extraction with hot pyridine resulted in a residue (75%) which is *more stable thermally* than the unextracted material.⁸

6. Phosphorus

Black phosphorus has been prepared at 16,000 and 25,000 atm. and 800°C.⁴

III. ORGANIC REACTIONS AND MATERIALS

1. 1,2,3,4,5-Pentafluorophenyl 1,2,3-Trifluorovinyl Ether

A yield of 2.7% of polymer has been obtained at 105°C and 12,000 atm., under γ -irradiation.³

2. n-Perfluoroheptene-1

Pressures of 11,000-15,000 atm. accelerate rate of polymerization by a factor of 30 over rate at 1 atm., under γ -irradiation. G-value for conversion of monomer to polymer *increases* with temperature at approximately constant pressure, and with pressure at constant temperature, with expectation of maximum between 200-300° at 12,000 atm. Polymer appears to have a high glass transition and is probably transparent in the ultraviolet.³

3. Perfluorocyclobutene

Polymerizes slowly with low yield at 25,000 atm. and 250°C, but not at 40,000 atm. and 200°C. Good yield results in use of hexafluoroacetone as solvent.⁴

4. Perfluoropropylene

Homopolymerized at temperatures of 200-300°C between 10,000 and 40,000 atm. using free radical catalysts; polymers melt between 250-315°C. In this pressure range there is *no effect on yield*.⁴

5. Propylene

Polymerization under pressure to 15,000 atm. and temperature to 83°C initiated by γ radiation proceeds by a *chain mechanism*. A free radical rather than an ionic mechanism is indicated. Propylene becomes more *difficult to compress* with increasing pressure and decreasing temperature; average intermolecular distance at 15,000 atm. is still considerably greater than normal bond lengths. Maximum conversion of monomer to polymer was 20%.²

6. n-Tetradecafluoroheptene-1

Samples of polymer prepared at 8,100 atm. under γ -irradiation flow at temperature of 100°C; those prepared at 17,000 atm. do not flow at 200°C. Maximum conversion of monomer to polymer is 15%. *Transfer* limits the molecular weight, the transfer constant apparently increases with temperature.³

7. 1,1,2-Trifluorovinylphenyl Ether

Under γ -irradiation, the monomer polymerizes more slowly at 145°C than at 102°C. At 191°C the *dimer* forms to the complete exclusion of polymer.³

REFERENCES

1. H.T. Hall, J.D. Barnett, Final Report, 1 June 60-30 May 62, Grant DA-ORD-42, Brigham Young Univ.
2. D.W. Brown, L.A. Wall, "Radiation-Induced Polymerization of Propylene at High Pressure." National Bureau of Standards (manuscript).
3. D.W. Brown, L.A. Wall, "The Radiation-induced Polymerization of n-Tetradecafluoroheptene-1; 1,1,2-Trifluorovinylphenyl Ether, and 1,2,3,4,5-Pentafluorophenyl 1,1,2-Trifluorovinyl Ether at High Pressures." National Bureau of Standards (manuscript).
4. W.H. Mears et al., Status Report No. 1, 1 May 62 - 30 Sept 62, Contract DA-30-069-ORD-3551, Allied Chemical Corp., General Chemical Div.
5. H. Eyring and A.F. Gabrysh, Status Report No. 2, 1 Apr 62 - 30 Sept 62, Grant DA-ARO(D)-31-124-G243, Univ. of Utah.
6. L.A. Wall et al., Status Report No. 1, 1 June 60 - 31 Mar 61, ARO(D) Proposal 2703, National Bureau of Standards.
7. L.A. Wall et al., Status Report No. 2, 1 Apr 61 - 30 Sept 61 ARO(D) Proposal 2703, National Bureau of Standards.
8. L.A. Wall et al., Status Report No. 3, 1 Oct 61 - 20 Apr 62, ARO(D) Proposal 2703, National Bureau of Standards.

Prepared by George B. Cox