Diaminomaleonitrile as a high-throughput precursor for alternative layered C=N-based conjugated polymers to carbon nitrides



In the present work, the fast production of C=N-based conjugated macrostructures from the bulk thermal polymerization of diaminomaleonitrile (DAMN) is discussed. These high-throughput syntheses showed air tolerance and were studied under different temperature regimes, from 160 to 200 °C, according to solid-state or melt polymerization (MP). This study displays not only the effect of temperature and exposure to air but also the gases evolved during the polymerization reactions. These volatiles were suitably analysed, providing relevant information about the elimination processes that take place during the course of these thermolytic reactions. The microstructure and physical properties of these black polymer materials obtained were determined by elemental analysis, Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) and ultraviolet-visible (UV-Vis) spectroscopies, X-ray diffraction (XRD), thermogravimetry (TG), electron paramagnetic resonance (EPR), electrochemistry measurements and scanning electron microscopy (SEM). The interpretation of all these data suggests that a two-dimensional (2-D) macrostructure based on N-heterocycles as diazines is predominant, regardless of the state of monomer aggregation during the course of the polycondensations. Interestingly, these 2-D polymeric systems present characteristic analogues with well-documented carbon nitrides $(g-C_3N_4)$, with similar magnetic, electrochemical, optical and catalytic properties. Thus, DAMN polymers are proposed as alternative materials to relevant $g-C_3N_4$, as their synthetic process is easy, quick and highly efficient.

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