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ADVANCES IN RADICAL COPOLYMERIZATION OF F-MONOMERS WITH CYANO COMONOMERS: SYNTHESIS, CHARACTERIZATION AND PROPERTIES

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High dielectric constant polymers are becoming crucial components in advanced electronic devices, such as memory and gate dielectrics for integrated circuits, stationary power generation, and miniature capacitors for telecommunication[1]. In this case, polymers containing polar substituents including fluoro and cyano groups are of interest in the development of advanced electrical because of the large dipole moment expected from the polar substituents.[2] Nonlinear optical, piezoelectric, and pyroelectric properties have been observed in the polymers.[3] Vinylidene cyanide (VCN) has often been employed in the preparation of high polar polymers as a useful starting monomer.[4,5]. Ferroelectric poly(vinylidene fluoride) and its copolymers are the most important dielectric polymers due to the polarization originating from C-F bonds and to the spontaneous movement of dipoles in the crystalline phases [6].

In the same way, many fluorinated (co)polymers have been studied for their outstanding properties (thermal stability, chemical inertness, low surface tension, good electric properties, and wire insulation) [7]. The performance of a series of acrylic-based copolymers as protective coating materials for stone or ancient buildings has been carried out by comparing them with unfluorinated polymeric analogues [8-9].

In this present work, we described synthesis, characterization and properties of three families of cyanofluorinated polymers:

1- Copolymers containing 2,2,2-trifluoroethyl methacrylate and cyano monomers (AN, MAN, VCN and MVCN) were synthesized by radical copolymerization initiated by AIBN. These copolymers were characterized by ^{1}H, ^{19}F and ^{13}CNMR as well as FT-IR spectroscopies [10]. Films of these copolymers have been studied using dielectric relaxation spectroscopy.[11]

2- The synthesis and the characterization of original copolymers based on vinylidene cyanide (VCN) and 1H,1H,2H,2H-perfluorodecyl vinyl ether (FAVE8) are presented[12] The radical copolymerization of VCN with FAVE8 unexpectedly led to alternating poly(VCN-*alt*-FAVE8) copolymers. Thermogravimetrie analysis showed that these copolymers are themostable, the thermal degradation starts from 350 ℃ (under air). Superhydrophobic and highly oleophobic surfaces were noted as evidenced by the water and diiodomethane Superhydrophobic and highly oleophobic surfaces were noted as evidenced by the water and diiodomethane contact angles.

3- Preliminary studies of the block copolymers (PVDF block, PVDF-b-PAN, PVDF-b-PMAN and PVDF-b-PVCN block copolymers) are presented. These copolymers are synthesized by ITP and have been characterized. DSC and TGA analyses have shown that the polymers were semi-crystalline and have high temperature stability, except for PVDF-b-PVCN[13]. The crystallinity of PVDF decreased, when cyano blocks were added. Their dielectric behaviors have been described and compared to similar copolymers to evaluate their dielectric properties. The incorporation of VDF units in the block copolymers improves the dielectric permittivities compared to those of cyano homopolymers: poly(AN, MAN or VCN).