

ABSTRACT

The unpaired electron spins have magnetic moments, which have a tendency to align itself in the direction of magnetic field (MF). The radical chain polymerization of vinyl monomers involving odd (unpaired) electrons is expected, therefore, to be influenced by the MF. Moreover, polar monomers may be influenced relatively to a greater extent than nonpolar monomers by the MF due to their diamagnetic anisotropy. As a result, the course of the entire polymerization process, its kinetics, and the micro- and macro-structure of polymers/copolymers prepared under MF, and hence their properties are expected to be influenced by the MF. In case of copolymerization of two vinyl monomers having different polarities, the copolymer composition, monomer reactivity ratios and the distribution of monomer sequence in the copolymer chain are also expected to vary under MF. With this objective different polymerization/copolymerization systems have been studied under MF in this investigation.

Different vinyl monomers like styrene (S), acrylonitrile (AN), acrylamide (AM), methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) have been polymerized/copolymerized using different initiating systems (viz., benzoylperoxide (BPO), 2,2'-azobisisobutyronitrile, cyclohexanone, redox initiators like BPO and dimethylaniline, hydrogen peroxide and thiourea) and conditions (viz., bulk and solution). A lyotropic liquid crystal (LC) polymer, poly(amide hydrazide) has also been synthesized by polycondensation at low temperature. The kinetics of polymerization is studied gravimetrically. In order to critically analyze the influence of MF on the initiation step

of radical polymerization, the decomposition of chain initiators, BPO and AIBN, has also been investigated. The decomposition of BPO has been measured by the iodometric titration of peroxide content and also by the spectroscopic method using 2,2 -diphenyl-1-picryl hydrazyl (DPPH) as radical scavenger. The decomposition of AIBN has been measured by the spectroscopic method using DPPH and also from the absorbance due to the -N=N- group of undecomposed AIBN. Regarding the structure and properties, the polymers/copolymers are analyzed by viscosity, density and dielectric property measurements, and GPC, IR, NMR, XRD, SEM and thermal analyses. X-ray photoelectron spectroscopy (XPS or ESCA) has also been utilized to determine the SAN copolymer composition and monomer reactivity ratios.

The MF influences the decomposition and/or radical generation from BPO but not from AIBN. The MF enhances the radicals available to be scavenged by DPPH due to the Δg -mechanism and cage effect. Therefore, the rates of vinyl polymerization (HEMA, styrene and AN copolymerization) using BPO as initiator are increased under MF.

The MF increases the radical and redox polymerization of AN. However, the radical polymerizations of styrene and MMA are not affected by MF. The effect of MF on the AN polymerization may be due to its heterogeneous nature of polymerization (occlusion theory), where the diffusion control termination by combination is hindered in the presence of MF. The molecular weight (MW) of polyacrylonitrile (PAN) increases whereas the molecular weight distribution (MWD) becomes narrower when PAN is prepared

under MF. The syndiotactic content of PAN is higher when prepared under MF. The PAN polymers obtained under MF are more stereoregular, crystalline and denser, and also having better dielectric behavior and thermal stability.

Triplet dye (methylene blue) sensitized photopolymerization of MMA is not influenced in aqueous medium whereas the rate of polymerization decreases and MW increases in water-methanol mixture by the application of MF. The photopolymerization of MMA using cyclohexanone as a biradical initiator is not influenced by MF.

The AN content in the SAN copolymer increases when prepared at low temperature under MF. Therefore, the kinetic factors controlling the copolymer composition i.e., the monomer reactivity ratio of AN increases whereas that of styrene decreases under MF. The glass transition temperature (T_g) of SAN copolymer obtained under MF is also higher.

The rate of condensation polymerization of a diamine and diacid chloride to form a LC polymer is not influenced by MF. However, higher MW and more thermostable LC polymer, poly(amide hydrazide) is obtained when prepared under MF.

Key words : Magnetic Field, Radical Polymerization, Copolymerization, Initiator decomposition, Dye-sensitized Photopolymerization, Polymer Properties.