

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

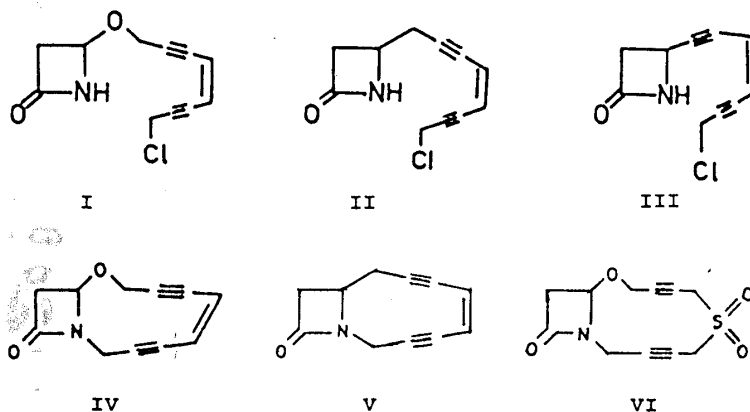
of radical polymerization, the decomposition of chain initiators, BPO and AIBN, has also been investigated. The decomposition of BPO has been measured by the iodometric titration of peroxide content and also by the spectroscopic method using 2,2-diphenyl-1-picryl hydrazyl (DPPH) as radical scavenger. 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

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Considerations of the biological mechanism of actions of the two well-known natural functionalities, β -lactam and enediyne, led us to design the following hybrid molecules:



Calculations on the bicyclic enediynes predicted rapid spontaneous cyclization of the ten membered enediyne, on the basis of distance theory of Nicolaou.

4-Benzoyloxy-2-azetidinone was shown to be a better (yield and costwise) synthon for the preparation of 4-heterosubstituted 2-azetidinones compared to the more widely used 4-acetoxy analogue.

Palladium (0) catalyzed ene-yne coupling has been successfully applied to the synthesis of azetidinyl acyclic enediynes I-III in respectable yields. Preliminary biological testing against ampicillin resistant *Echerichia coli* gave encouraging results. The enediynes II and III were found to have stronger activity when compared to oxytetracycline at similar concentrations.

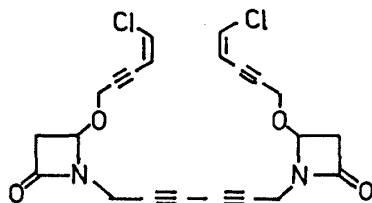
Bicyclic azetidinyl enediynes IV and V have been synthesized for the first time by a novel N-C alkylation. Their exceptional thermal stability is in agreement with the fact

that the β -lactam is probably acting as a lock in stabilizing the otherwise reactive enediyne system.

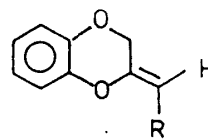
Various other Pd(0) catalyzed reactions on β -lactams yielded novel products. The most notable among them is a novel bis-azetidinone derivative (VII).

Azetidinyl bis-propargyl sulphone (VI) has been synthesized. The role of the β -lactam ring acting as a lock in preventing isomerization of propargyl to allene has been demonstrated by comparing with the behaviour of other bispropargyl sulphones (VIII) and (IX) derived from catechol and alizarin and alizarin.

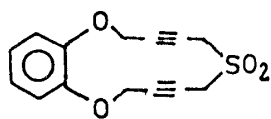
A Pd(0)-based high yielding regio and stereoselective method for the preparation of benzodioxan derivatives (X), one of which (R = CH₂OH) is an intermediate for the antidepressant drug azaloxan, has been developed.



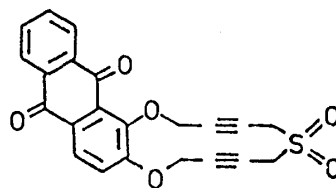
VII



X



VIII



IX