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The synthesis, characterization and study of biodegradation of polymers are a center of attraction to scientist as well as technologist belonging to several disciplines such as chemistry, biology, medicine and agricultural sciences. For many biomedical, agricultural and ecological purposes it is desirable to have a biodegradable polymer that will undergo degradation in the physiological or by the microbial action in the soil. Hence, it is important to mimic with the synthetic polymers which show some of the remarkable adaptations (among them one is biodegradability) of the biopolymers. The research on such polymers is useful to both academics and to industrial scientist.

The present work described in this thesis mainly deals with synthesis, characterization and studies of properties of polymers. These polymers are homopolymer of acrylamide (AM), acrylic acid (AA), acrylonitrile (AN), N-vinyl pyrroidone (VP), vinyl acetate (VAc), styrene (S), methyl acrylate (MA), methyl methacrylate (MMA), ethyl acrylate (EA), butyl acrylate (BuA), *n*-hexyl acrylate (HA), cyclohexyl acrylate (CA), benzyl acrylate (BA) and their copolymers / tercopolymers in different monomer feed ratios. The polyamides based on diacid (i.e. tartaric acid) with various diamines viz. ethylene diamine, hexamethylene diamine (HMDA) and benzidine were also synthesized. The knowledge of the characterization and properties of these polymers play an important role in determining the industrial end products. The different physicochemical and microbiological methods involved in the studies of polymer properties were swelling behaviour, viscosity measurement and preliminary testing of biodegradability.

The synthesis of '*tailor made*' polymers to meet specific requirements has gained importance in recent past. These polymers were synthesized by the free radical solution / microemulsion polymerization process. The polymers are PAM, PAA, PAN and tercopolymers of AM, AA and AN; PVP, PVAc and copolymers of VP and VAc; PS, PMA, PEA, PBuA, PHA, PCA, PBA, PMMA and copolymers of the monomers with S and VAc. Besides this, polyamides of diacid with various diamines in different feed ratios were synthesized by condensation process. They were characterized by spectroscopic techniques like FTIR, ^{1}H- and ^{13}C-NMR; elemental analysis; thermal methods such as TGA, DSC, SEM, WAXD and GPC measurement. Knowledge of the successive addition of monomer units in case of homo-, co- and tercopolymers, configurational and compositional structure of chains, sequence distribution can be obtained by spectroscopic characterization. Elemental analysis data help to evaluate actual composition of the resulting copolymers / tercopolymers.

The IR spectra of the homo-, co- and tercopolymers showed absorption bands characteristic of constituent monomeric units with their relative intensities depending on composition thereby proving the formation of homo-, co- and tercopolymers. The IR spectrum of PAN showed characteristic absorption at 2246 and 1452 cm^{-1} due to the nitrile group. The C=O of PAA was observed at 1738 cm^{-1} and the broad absorption band due to the O-H of the –COOH group was observed around 3300 cm^{-1}. The C=O band of the carbonamide group (i.e. –CONH$_2$ of PAM) showed strong absorption band at 1650 cm^{-1} and the medium absorption at 1400 cm^{-1} was due to the C-N stretch. The characteristic absorption peaks due to all three functional groups were present in all the tercopolymers studied and their relative intensities depending on composition.

In case of PVAc, the band at 1061 cm^{-1} is associated with the isotactic structure of the polymer. The prominent absorption peaks were at 617 cm^{-1} and 1734 cm^{-1} due to the out-of-plane CH_2-CO_2 and C=O band, respectively. PVP showed strong absorption at 1654 cm^{-1} is associated with the C=O absorption of tertiary amide and the five-membered ring. The C-N stretching absorption appears at higher frequency (1283 cm^{-1}) than the normal aliphatic amine. The infrared spectra of P(VP-VAc) and P(VP-VA) copolymers also showed absorption bands typical of constituent monomeric units.

Further evidence for the two / three monomers being incorporated in copolymers / tercopolymers was obtained from NMR spectra. Both the ^{1}H-NMR and ^{13}C-NMR spectra are complimentary to each other. The ^{1}H-NMR spectra of tercopolymers P(AM-AA-AN) showed a broad peak in the range of δ=1.4–2.0 ppm due to methylene groups of acrylamide unit. A sharp peak was observed due to the methine of the acrylic acid comonomers at δ=2.75 ppm and δ=2.93 ppm due to the acrylonitrile comonomer.

For the case of copolymers P(VP-VAc), ^{1}H-NMR spectra showed resonance signals at δ=4.77 ppm and in the region of δ=3.75-3.95 ppm due to methine back bone protons of VAc and VP, respectively. Three peaks that occur at δ=1.98, 2.00 and 2.02 ppm are associated with the acetoxy proton signals of VAc monomeric unit.

PS homopolymer resonance signals appeared at δ=7.05-6.52 (benzene ring), 1.85 (αCH-) and 1.43 ppm (βCH_2-), whereas 7.21 (benzene ring), 4.93 (-CH_2- adjacent to phenyl group), 2.35 (αCH-) and 1.62 ppm (βCH_2-) are the resonance signals corresponding to PBA. In the case of PCA, the signal appear at δ=4.70 ppm associated with proton of –OCH group and resonance signals appeared at 1.76 and 2.25 ppm are due to five methylene groups of cyclic ring. The methine and methylene back bone protons resonate between δ=3.69-3.63 and 1.38 ppm. All the copolymers of styrene and vinyl acetate with various acrylates showed signals at their expected respective positions and the change in the intensity of the peaks was observed as expected.

The ^{13}C-NMR spectrum of PAN giving rise to multiplet signal in the region δ=119.53-120.17 ppm due to nitrile (-CN) carbon. The PAA shows three well resolved peaks in ^{13}C-NMR at δ=176.4, 39.13 and 31.91 ppm corresponding to carbonyl, methine and methylene carbon, respectively. Besides these, the ^{13}C-NMR spectra of tercopolymers consisting two distinct signals at δ=175.95 and 174.30 ppm due to carbonyl signals of $-CONH_2$ and –COOH groups, respectively. As the ratio of AN and AA increases, the intensity of the peak height increases in the expected direction.

In ^{13}C-NMR, signals due to the carbons of long alkyl side chains were observed in the region δ=14-42 ppm. The assignment of various resonance peaks due to different carbon atoms were done using the additive shift parameters for hydrocarbons. The calculation of shift were done using the formula, the shift parameter $\delta = 2.5 + \Sigma\, nA$, where A is the additive shift parameter and 'n' is the number of carbon atom for each shift parameter. For PHA, δ was predicted for all the five side-chain carbon atoms and was observed at 13.8, 22.9 and 32.0 ppm. The $-OCH_2-$ group showed resonance at 64.9 ppm. The observed values were in good agreement with the calculated values. Besides, the methine, methylene and carbonyl groups resonated at 41.6, 35.6 and 174.4 ppm, respectively.

The composition of the copolymers / tercopolymers were obtained by elemental analysis and NMR spectroscopic technique. Various equations were used to determined the composition of these polymers. The mole fraction of VP (m_1) in the copolymer [P(VP-VAc)] was determined using the relation

$$m_1 = \frac{I\,(\text{-CH of VP})}{I(\text{-CH of VP}) + I(\text{-CH of VAc})} \qquad (\text{for } ^1\text{H-NMR})$$

where m_1 is the mole fraction of N-vinyl pyrrolidone (VP), I(-CH of VP) and I(-CH of VAc) represent the peak intensities of –CH protons of VP (resonated at 4.77 ppm) and VAc (resonated at 3.75-3.95 ppm), respectively.

The following relation was used to determined the mole fraction of styrene (m_1) in the P(S-CA) copolymer

$$m_1 = \frac{A_{ph}}{A_{ph} + 5A_{\text{-OCH}}} \qquad (\text{for } ^1\text{H-NMR})$$

where A_{ph} and $A_{\text{-OCH}}$ represent the ^{1}H-NMR resonance peak areas of protons of phenyl (~7.0 ppm) and –OCH (~4.48 ppm) groups, respectively.

The styrene mole fraction (m_1) in the P(S-BA) copolymer was evaluated using the distinct peaks of methylene protons (~4.57 ppm, adjacent to phenyl group of BA unit) and the peak intensity corresponds to the total number of protons (10 protons in BA and 8 protons in styrene) of a particular group.

The expression used is

$$\frac{\text{Intensity of methylene proton } (I_{CH2})}{\text{Intensity of total protons } (I_T)} = \frac{2\,m_2}{10\,m_2 + 8\,m_1}$$

From the above equation and $m_1 = 1 - m_2$, the following relation was derived for composition calculation

$$m_2 = \frac{4\, I_{CH2}}{I_T - I_{CH2}} \qquad \text{(for } ^{1}\text{H-NMR)}$$

where m_2 is the mole fraction of BA in the P(S-BA) copolymers.

Using ^{13}C-NMR data, mole fraction of VP(m_1) in the P(VP-VAc) copolymers was also evaluated by the expression :

$$m_1 = \frac{I\,(C{=}O \text{ of VP})}{I\,(C{=}O \text{ of VP}) + I\,(C{=}O \text{ of VAc})} \qquad \text{(for } ^{13}\text{C-NMR)}$$

where I (C=O of VP) and I (C=O of VAc) represent the peak intensity of carbonyl carbons of VP and VAc monomeric unit, respectively.

Using the experimental feed ratios of various monomers as well as the composition of the resulting copolymers (obtained from the elemental analysis and spectroscopic data), reactivity ratios of the monomers in the copolymers were estimated. The graphical methods of Fineman-Ross (F-R) and Kelen-Tudos (K-T) were used for such calculation. The reactivity ratios for monomer-1 (i.e. VP, AA+AN, S) and monomer-2 (i.e. VAc, AM, CA or BA) were determined by the F-R method. The values obtained for various pairs of monomers are r_1(VP) = 0.174 and r_2 (VAc) = 0.137 for copolymers of P(VP-VAc), r_1 (AA+AN) = 0.86 ± 0.05 and r_2 (AM) = 1.94 ± 0.09 for tercopolymer P(AM-AA-AN), r_1 (S) = 0.930 and r_2 (CA) = 0.771 for P(S-CA) copolymer, r_1 (S) = 0.755 and r_2 (BA) = 0.104 for P(S-BA) copolymer, r_1 (VAc) = 0.089 and

r_2 (CA) = 1.109 for P(VAc-CA) copolymer, r_1 (VAc) = 0.155 and r_2 (BA) = 0.390 for P(VAc-BA) copolymer, respectively.

The reactivity ratios for the copolymers were also determined by the K-T method and the corresponding r_1 and r_2 values obtained for various monomer pairs are r_1(VP) = 0.189 and r_2 (VAc) = 0.169 for P(VP-VAc) copolymer synthesized in solution, r_1 (AA+AN) = 0.86 ± 0.009 and r_2 (AM) = 1.93 ± 0.03 for tercopolymer P(AM-AA-AN), r_1 (VAc) = 0.089 and r_2 (CA) = 1.109 for P(VAc-CA) copolymer and r_1(VAc) = 0.164 and r_2 (BA) = 0.461 for P(VAc-BA) copolymer, respectively.

Using reactivity ratios data, the statistical distribution of the monomer sequences M_1-M_1, M_2-M_2 and M_1-M_2 were obtained. Mean sequence lengths μ_1 and μ_2 were computed for the copolymer systems. For the series of tercopolymers of (AA+AN) and AM studied, μ_1 varied from 1.1 at 0.14 / 0.86 mole ratios of (AA+AN) / AM in the tercopolymer to 4.1 with a 0.78 / 0.22 mole ratios. The calculated mole ratios and r_1r_2 values indicates that the tercopolymers are block copolymers of AM and (AA+AN) which are rich in AM.

The copolymer composition vs initial monomer composition plot was sigmoidal and it crossed the ideal line at the point where $M_1 = m_2 = 0.766$ and 0.785 for P(S-CA) and P(S-BA) copolymers respectively, indicating the azeotropic copolymer composition for these systems. The experimental reactivity ratio values were also used to determine *Q* and *e* values for CA and BA monomers. The Alfrey-Price *Q*, *e* scheme were used for such calculation and the computed values were found to be $e_1 = 1.38$ and $Q_1 = 0.19$ for CA and $e_1 = 0.80$ and $Q_1 = 0.37$ for BA monomers, respectively.

Thermal analysis of the polymers were done by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis. Thermograms of the copolymers / tercopolymers fall in between those of the respective homopolymers implying that the thermal stability of copolymers / tercopolymers is in between the homopolymers. Two stage decomposition was observed in all polymers except polyacrylamide (PAM) which showed a three stage decomposition and poly(vinyl acetate) (PVAc) which showed one stage decomposition. The activation energy associated with different stages of decomposition of polymers were evaluated by using well-known methods of Broido's, van Krevelen, Anderson-Freeman (A-F) and PPS eqn. using single thermogram. Multiple heating rates method like that of Ozawa and Reich were also used to calculate activation energy of decomposition.

DSC thermogram for various homo-, co- and tercopolymers were recorded at 10°C min^{-1} to obtain glass transition temperature (T_g), onset temperature (T_o) and peak temperature (T_p) for the endotherm. It is observed that polyacrylate have low values of T_g but as the styrene units are incorporated in the copolymer with acrylate, enhancement in T_g values was observed. This is due to specific interaction between the two monomeric units present in the copolymers. DSC data of tercopolymers implying that all the tercopolymers have almost similar structure of polymer backbone and a limited branching in the main chain.

Swelling is a measure of interaction between polymer chains and the solvent molecule. The swelling data of P(VP-VAc) copolymers indicated that the percent swelling increases with increase of the VAc content in the copolymer up to around 0.7 mole fraction before it decreases in all solvents. This is due to the fact that as the concentration of VAc in the copolymer increases the density decreases up to about 0.7 mole fraction and hence, the polymer structure become highly porous with increasing VAc. This, in turn, accepts more solvent and, hence, higher swelling. With further increase in the VAc concentration, the copolymer structure become more condensed and, hence, there is less swelling.

Intrinsic viscosity $[\eta]$ was different at different temperatures in different solvents, for each of the polymers. The $[\eta]$ values of the homo- and copolymers were evaluated. The tercopolymers of AM, AA and AN in different monomer feed ratios, showed polyelectrolyte like behaviour in water, DMF and a mixture of water : DMF. η_{sp} for these systems increases with dilution contrary to the behaviour of nonionic polymers. For such systems, intrinsic viscosity was determined using the following empirical relation.

$$\eta_{sp} / C = A / (1 + BC^{1/2})$$

where A and B are constants. A straight line was obtained on plotting $(\eta_{sp}/C)^{-1}$ against $C^{1/2}$ and '*A*' represents the intrinsic viscosity $(\eta_{sp}/C)_{C\to 0}$. Viscosity average molecular weight M_v of PVP, PVAc and their copolymers were evaluated using Mark-Houwink relationship : $[\eta] = KM^{\alpha}$, where reported values of K and α in chloroform, 19.4×10^{-3} and 0.64 respectively, were used. Other parameters like K'-K", voluminosity (V_E), shape factor (ν), activation parameters of viscous flow, root mean square end-to-end distance ($\langle R^2\rangle^{1/2}$), radius of diffusing particle (r') and diffusion coefficient (D_o) were also calculated. K'-K" values are generally 0.5 for a good solvent system. The values obtained are ~0.5 for most of the systems. The V_E values decrease with increase in temperature indicating desolvation. The shape factor values are also found to be ~2.5 suggesting macromolecules acquire a spherical conformation in solution. The $\Delta H^{\neq}_{vis}/R$ and $\Delta S^{\neq}_{vis}/R$ values were found to be constant quantities independent of temperature implying that the polymers in solvent systems are not cross-linked and the structure of the homopolymers and copolymers are similar. The $<R^2>^{1/2}$ values decreases with increase in temperature indicating coiling of the polymer chain in solution whereas r' was found to be independent of temperature.

Biodegradation studies of vinylic tercopolymers [TP-1, TP-2 and TP-3] of AM, AA and AN and a polyamide of tartaric acid and ethylene diamine were carried out in a minimal medium using gram negative, rod shape soil isolate BA-1 and TED-1. Biodegradation was evaluated by following the polymer dependent growth turbidimetrically and by estimating the whole cell protein. In case of tercopolymer, polymer dependent respiratory activity was also measured.

For both the polymers, for the growth of isolate BA-1 and TED-1, the presence of the polymer in the minimal medium was found to be essential. The isolates did not grow in the absence of the polymer in the synthetic medium. Growth retarding ability of the polymers in the vinylic series was found to be in the order TP-3 > TP-2 > TP-1 due to the increase in the proportion of acrylonitrile in the tercopolymer and thereby decreasing the susceptibility towards biodegradation. This observation was further supported by decrease in polymer dependent respiratory activity in the above order. Thus, the above microbiological observation suggested that these polymers were used as growth substrate and thereby indicated biodegradable nature of these polymers.