Synthesis and Evaluation of Some Polymeric Compounds

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Polymer science was born in the great industrial laboratories of the world of the need to make and understand new kinds of plastics, rubber, adhesives, fibers, and coatings. Only much later did polymer science come to academic life. Perhaps because of its origins, polymer science tends to be more interdisciplinary than most sciences, combining chemistry, chemical engineering, materials, and other fields as well.Chemically, polymers are long-chain molecules of very high molecular weight, often measured in the hundreds of thousands. For this reason, the term “macromolecules” is frequently used when referring to polymeric materials. The trade literature sometimes refers to polymers as resins, an old term that goes back before the chemical structure of the long chains was understood.The first polymers used were natural products, especially cotton, starch, proteins, and wool. Beginning early in the twentieth century, synthetic polymers were made. The first polymers of importance, Bakelite and nylon, showed the tremendous possibilities of the new materials. However, the scientists of that day realized that they did not understand many of the relationships between the chemical structures and the physical properties that resulted.The structural units of a polymer chain are normally closely related to the structure of the starting material or monomer from which the polymer is prepared. The simplest linear polymers are those in which all structural units are identical ; such materials are called homopolymers, whilst polymers incorporating two or more chemically different types of structural units into the chain are termed copolymers. The majority of synthetic copolymers contain only two types of structural units and are therefore termed binary copolymers.If, however, some of the monomer molecules are trifunctional, i.e. capable of bonding to three other untis, then the polymer may have a non-linear structure which may be represented as follows:X-M............. M-T-M.............. M-X|M::M|X(I)A polymer of this form, in which the structural units of the side chain are identical to those of the main chain (or backbone), is said to be branched.If the side-chains of a branched polymer are formed from structural units which are different from those of the backbone, the polymer is termed a graft copolymer. A side chain in a branched polymer may be terminated either with a monofunctional end-group, or by reaction with a trifunctional unit in another chain. In the latter case two chains become joined by a crosslink. If crosslinking becomes extensive, the polymer form networks which may be two- or three dimensional. The formation of three dimensional networks during polymerization results in a cross-linked network which forms a gel fraction, insoluble in solvents appropriate for the noncross-linked material.Free-radical -copolymerizationFree-radical copolymerization may be defined as a process where by two or more monomers are integral parts of a high polymer via radical chain reaction.A copolymer is the product resulting from such a process. The importance of the free radical copolymerization, is a method for modifying the properties of polymers. Hard polymers, as for example, polyvinyl chloride, can be made softer, by copolymerization with monomers whose homopolymer are rubber like, such as vinyl ether or acrylic esters.Copolymer composition equationThe composition of the copolymer molecules which are formed at a given time in a mixture of two monomers depends on the relative rates with which the two kinds of monomer units enter a copolymer molecule. When the rate at which a monomer adds to the polymer chain depends only on the monomer unit at the end of the chain and not on the next-last monomer unit (penultimate), the composition of the copolymer is determined by the molar composition of the mixture of the monomers and by the rate constants of the following four reactions 1, 2:where K11 is the rate constant for the reaction in which monomer M1 adds to a radical chain ending in M1, K12 is the rate constant for the reaction in which monomer M2 adds to a radical chain ending in M1….etc. The composition of the copolymer that is formed could be related to the concentration of the two monomers in the feed as follows:from the copolymerization reactions (1-4), M1and M2 are used in the reaction as :-d [M1]/dt = K11 [M1] [M2] + K21 [M2] [M1] ... ... (5)-d [M2]/dt = K22 [M2] [M1] + K12 [M1] [M2] … … (6)The ratio of the amounts of the two monomers incorporated into the copolymer in an infinitesimal period of time is given by dividing equation (5) by equation (6) to get:d[M1] [M1] K11 [M1] [M2] + K21------- = ---- . ------------------------- … … (7)d[M2] [M2] K12 [M1] [M2] + K22The ratio K11/K12 and K22/K21 are defined by r1 and r2, respectively, and termed the monomer reactivity ratios which measure the relative affinities of different monomers for the same radical. At the steady state, for M1 and M2 to remain constant, their rate of interconversion must be equal, i.e.K21 [M2] [M1] = K12 [M1] [M2]Substituting this result in equation (7) gives the copolymer composition equation as:d [M1] [M1] r1 [M1] + [M2]-------- = ------ . --------------------- … … … … (8)d[M2] [M2] r2 [M2] + [M1]This equation relates the copolymer composition to the commoner concentration in the feed.The copolymerization equation can also be rearranged in terms of mole fraction instead of concentration as [3]:r1 $f^2$1 + f1 f2F1 = ---------------------------------- … … …. (9)r1 $f^2$1 + 2f1f2 + r2 $f^2$2where : F1 = mole fraction of monomer M1 in copolymerandf1 = mole fraction of monomer M1 in feed.Types of copolymerization behaviourfrom the copolymerization equation (1-4,P. 4), if K11>K12 andK22>K21 copolymerization would be insignificant and a mixture of homopolymers or block copolymer should be obtained , while if K12> K11 and K21> K22 this will lead to the formation of copolymers with an alternating sequence. If K12=K11 and K21 = K22 , the frequency with which M1 or M2 add to the chain end is determined by their concentration leading to an ideal copolymerization. These copolymerization can also be classified on whether the product of the two monomer reactivity ratios r1r2 is unity, less than unity, or greater than unity as follows:a- When r1r2 = 1, the two types of propagating species M1 and M2 show the same preference for adding one or the other of the two monomers, and the monomer units will be incorporated in a random manner influenced by the feed composition. Thus, substituting r2 = 1/ r1 in equation (8) and (9) one get:d[M1] [M1]------- = r1 ------ … … … … … … … (10)d[M2] [M2]andr1 f1F1= 1, this is a rare case and if it exists, it leads to the ------------r1f1 + f2b- When r1r2 synthesis of blocks of copolymers or a mixture of the homopolymers.Methods of calculating monomer reactivity ratiosAll methods for the determination of monomer reactivity ratios involve the experimental determination of the copolymer composition formed from several different feed composition. The techniques used for quantitative determination of copolymer composition include elemental analysis, radioisotopic labelling and ultraviolet, infrared and nuclear magnetic spectroscopy. All procedures depend on copolymerizations carried out to low degrees of conversion (less than 10%), and the experimental data can be analyzed in several ways. The more established procedures involving determination of monmer reactivity ratios are:Intersection methodThis method, originated by Mayo and Lewis4, depends of the copolymerization equation (equation 8, page 5) , which can be expressed in terms of molar ratios instead of concentration as4:r1 a + 1b = --------------------r2/a + 1where a and b are the molar ratios of the comonomers in the feed and copolymer, respectively. In this method, for each single copolymerization result, r1is allowed to take a selected value in the copolymerization equation, and r2 is plotted as a function of r1.The straight line corresponding to each experimental result should intersect at a common point giving the r1 and r2 values.Fineman-Ross methodFineman and Ross5 were the first who arrange the differential copolymer composition equation in the following forms:a a^2a - --- = r1 ------ - r2b bPlotting a-a/b as the ordinate against a^2/b as the abscissa, the slope of the straight line is r1 and the intercept is –r2. When the polymer composition measurements are precise, this method is very convenient and frequently used due to its simplicity and accuracy.Joshi-Kapur method6This method is published in 1954 with a view to eliminating subjective error in the location of the best point in the intersection method of Mayo-Lewis plot.Tidwell-Mortimer methodIn detailed critical treatises, Tidwell and Mortimer7 pointed out the defects of the different methods, and suggested a standard computerized procedure; the nonlinear least square method. This method presumes that there is no possible experimental error in the independent variable; the monomer composition of the feed; and that the absolute -error in the copolymer composition is independent of its value or constant.Yezrielev Brokhina-Roskin methodYezrielev, Brokhina and Roskin8 transformed the linear equation of copolymer composition into the symmetrical form as :a/b½ . r1- b½/a . r2 + (a/b½ - b½) = 0where a= M1/M2 (molar ratio of the two monomers in thecomonomer mixture).And b = m1/m2 (molar ratio of the two monomers in thecopolymer).In this method the theoretical line is situated evenly between the experimental points of positive and negative error which leads to determination of reactivity ratios more accurate.Kelen-Tudos methodThis is the most recent method published by kelen and Tudos9 for calculating the monomer reactivity ratios based on a new graphically valuable linear equation as follows:#NAME?a2= ------------α b + a2where:a (b-1)#NAME?αb + a2aminxamaxα = ----------------------(bminxbmax)½The variable cannot take any positive value, only those in interval of 0-1 Thus, plotting the values as the function of = 0 to = 1 gives – r2/α and r1, respectively (both as intercepts).Factors affecting monomer reactivity ratiosWith respect to free-radical copolymerization, it may be stated that reactivity ratios are comparatively little influenced by most common variables such as conversion, solvent and method of polymerization10. In the range of temperatures from room temperature to about 100°c there is little variation in reactivity ratios in binary copolymerizations.However, there is a tendency for the r1r2 product to approach 1 as temperature increases. Copolymerization has been affected at temperatures as -70°c and temperatures as high as 130°c, with large change in reactivity ratios. With respect to the solvent , numerous studies have been made which indicate that a change of solvent has little effect on monomer reactivity ratios. Accordingly, a highly polar or nonpolar solvent, does not appear to influence the value of reactivity ratios. The effects of dilution on reactivity ratios have been studied and it has been -concluded that no substantial effect exists. Also, polymerization by solvent nonsolvent techniques gives reactivity ratios similar to those of homogeneous system, that is the precipitation of copolymers during polymerization does not alter reactivity ratios. Monomer reactivity ratios have also been found to vary with pressure, for example, copolymerization of methyl methacrylate and acrylonitrile11,the product of r1r2 increased from 0.16 (at atmospheric pressure) to 0.91 (at 1000 atmosphere) indicating that increased pressure increases the tendency for this system towards blocks.Individual Monomer Reactivity In CopolymerizationIn a copolymerization reaction the reactive end of the growing chain is a free radical derived from one of the two monomers. Obviously, two type of reactive ends can exist and for this reason, reactivity ratios must be determined in pairs. Moreover, because the values obtained experimentally are relative values, the reactivity ratios must be determined experimentally for each pair of monomers. A correlation procedure that permits the assignment to each monomer of a reactivity parameter that is applicable to its copolymerization with all other monomers would represent a great economy in data accumulation and tabulation. One approach to developing such correlation takes into account the resonance and polar factors inherent in the monomers and is called the Alfrey-Price Q-e realtionship12. Q is a measure of the resonance stability of a monomer in copolymerization, and e is a polar factor. The fundamental equations are given as :r1 = (K11/K12) = [Q1/Q2] exp. [-e1 (e1 – e2)] (12)r2 = (K22/K21) = [Q2/Q1] exp. [-e2 (e2 – e1)] (13)r1r2= exp[- $(e1 – e2)^2$] … … … … … … … (14)In r1r2 =- $(e1 –e2)^2$… … … … … … … … (15)Price chose styrene as the standard monomer with the values Q=1 and e= -0.8. The Q and e values of any monomer that has been copolymerized with styrene can be calculated from the r1 and r2 values given in literature. Conversely, knowing the Q and e for any two monomers the r1 and r2 values can be calculated for this monomer pair, whether or not they have ever been copolymerized. While the predicted behaviour is not always exactly like the experimental result, the Alfrey-Price Q-e scheme nevertheless leads at least to a good approximations. The major shortcoming of the Q-e scheme is that all radical polymerization involve not only resonance and polar factors, but also steric factors. It is certainly conceded that steric factors limit the applicability of the scheme which is considered as an empirical method of correlation.