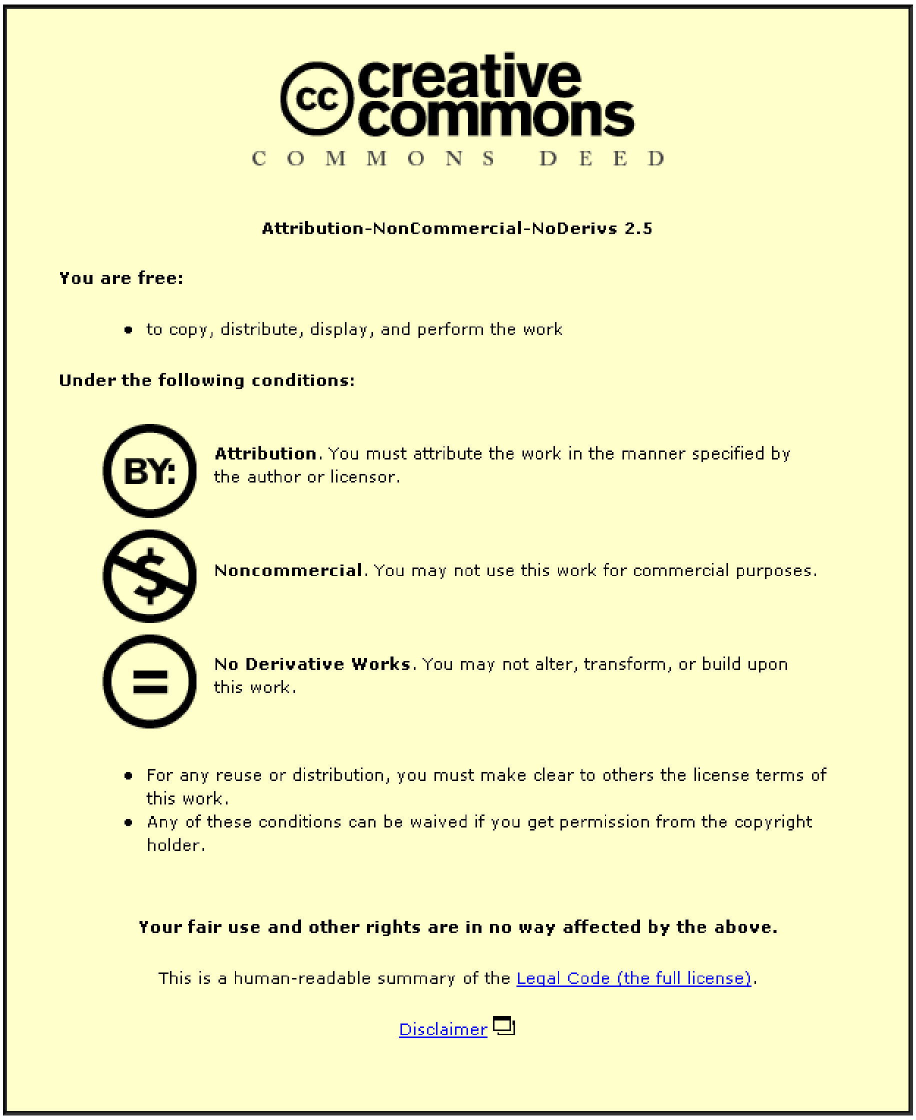

SOME POLYMER BLENDS AND BLOCK COPOLYMERS:
PREPARATION AND PROPERTIES.

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SUMMARY.

The solubility of polymers in caprolactam and laurolactam at 150°C was studied, results being discussed in terms of polymer solubility parameters, hydrogen bonding and polymer crystallisation.

Polymers soluble up to 10% by weight were dissolved in the monomers which were then polymerised by an anionic mechanism. Polysulphone and polycarbonate acted as cocatalysts in polymerisation of caprolactam, copolymers being formed. For all the other polymers polymerisation of the monomers resulted in polymer blends.

The effects of catalyst concentration, polysulphone concentration and polymerisation time on the preparation of polysulphone-polycaprolactam copolymers was studied. Copolymer composition, density and the molecular weights of the polysulphone components of the copolymers were determined. A reaction mechanism is proposed which agrees with other work published subsequent to the present study.

Optical microscopy showed that the phase structure of the copolymers changed continuously as the polysulphone concentration was increased. Phase inversion occured when the polysulphone concentration was increased from 5 to 10% by weight. Although the continuous phase appeared to be all polysulphone, staining showed it to contain some polycaprolactam.

Some physical properties of the copolymers were compared with those of commercial nylon 6. The results indicated that they could be suitable for fibre forming.

Polymer blends were prepared by polymerising caprolactam in the presence of polystyrene, impact styrene and S.B.S. thermoplastic rubber. Polycaprolactam homopolymers were prepared with various catalyst and cocatalyst concentrations.

As the concentration of the second polymer in the blend was increased their appearance suggested that the components were incompatible.

Optical microscopy showed that before moulding, some of the dispersed phase particles contained polycaprolactam arising from inversion or inclusion during polymerisation. Moulding resulted in a more clearly defined two phase structure.

Some physical properties of the blends were compared with those of the homopolymers. None of the blends had balances of properties which were as good as those of the homopolymers. Blends with polystyrene and impact styrene had the best tensile properties, those with thermoplastic rubber the best impact properties. The overall physical properties changed adversely as the concentration of the second polymer was increased, in line with the observed incompatibility of the components.

CONTENTS.

1. INTRODUCTION.

1:1 HISTORICAL.

It is now generally accepted that most of the major advances in commercial polymers will be through improvements associated with existing polymers. Polymer blends are expected to play an important part in this development. A polymer blend is defined as a single entity of material containing within its boundary at least two thoroughly mixed polymers which are not extensively linked together by covalent bonds.

Although the first recorded preparation of a polymer blend was in 1912[1] it was not until the late 1940's that they started to become commercially significant. One of the first commercial polymer blends, an impact resistant polystyrene containing 5% styrene-butadiene rubber, was introduced by Dow Chemicals in 1948. Today both homogeneous and heterogeneous polymer blends have become established in the field of commercial polymers. Homogeneous blends are used primarily to improve processing and heterogeneous blends for imparting toughness. Both have been used to a lesser extent to reduce the amount of a more expensive material.

1:2 PREPARATION OF POLYMER BLENDS.

Polymer blends can be prepared in several ways and these include mechanical mixing on rubber mills or in extruders, by coagulation of mixtures of polymer latices and from mixtures of polymer solutions or dispersions, sometimes involving polymerisation of one of the components.

The simplest and most direct way of preparing polymer blends is by mechanical blending on a two roll mill or in a Banbury Mixer, or more recently by hot mixing of powders followed by extrusion.

The nature of the resulting blends depends on the length of mixing, the shear forces in the mixing equipment and the rheological properties of the polymers. There is also the possibility of chemical effects produced by the mixing operation and it is well known that shearing polymers can result in chain scission. Not only does this generally affect the molecular weight, and hence change the properties of the individual components, it is also possible that the free radicals formed by chain scission can recombine to form block and graft copolymers. Angier and Watson[2] have mixed polymers under severe conditions and have analysed the products. When natural rubber and neoprene were mixed at a low temperature, and under a high shear force, the product was found to contain a complex mixture of block, graft, and cross-linked copolymers.

This method of preparing polymer blends is used for systems in which little thermal degradation occurs and is used throughout industry for preparing rubber-rubber mixtures and also rubber-plastic blends, such as those of nitrile rubber (NBR) with polyvinyl chloride(P.V.C.)

When the individual components can be obtained in latex form they may conveniently be mixed by blending the latices[3,4] This is another of the important techniques used in the preparation of commercial polymer blends. In a latex the polymers are present as suspended microspheres and interactions of neighbouring spheres is prevented by the suspending medium. This allows direct control of the particle size of the disperse phase without affecting the properties of the individual component phases.

After blending, the solid polymer blend is recovered by coagulation or spray drying. Polymer blends prepared by this method include polystyrene/styrene-butadiene rubbers (SBR) and acrylonitrile-butadiene-styrene (ABS) resins.

After such treatment melt processing is often employed to produce forms such as pellets but precautions must be taken at this stage to avoid degradation or undue change in the state of subdivision. In some latex blended polymers, e.g. certain mixtures of rubbers with plastics, which at first seem to be homogeneous, the components may have such a low affinity for each other that separation occurs during this process, reducing the value of the product.

It should also be possible to prepare polymer blends from homogeneous solutions of two polymers in a common solvent. There are difficulties in preparing homogeneous solutions, and also in recovering the solid polymer without destroying the structure of the blend. The solid polymer can be recovered by precipitation, by cooling, or the use of a non-solvent, or by drying. The solvent power of the solvent towards the two polymers will vary with temperature and it is unlikely that the precipitating effect of a non-solvent will be the same for both polymers. Cooling, and precipitation by the use of a non-solvent are therefore likely to lead to phase separation. Similar problems may also be encountered if the solvent is removed by drying but this technique should be more satisfactory than the other two.

Even though polymers must be compatible for the formation of a homogeneous solution, even more stringent conditions are necessary for the retention of the mixed state during the recovery of the solid polymer. Despite these difficulties compatible polymer blends which can be prepared by this method include polyvinyl acetate (PVAc)/polymethyl methacrylate (PMMA); nitrocellulose/PVAc and nitrocellulose/PMMA i.e. as special lacquers or films.

Other methods for preparing polymer blends produce two phase systems which are generally intended, in addition to providing good dispersion, to produce some copolymerisation. The less critical compatibility conditions for mixing a polymer with a low molecular weight material, either monomer or a prepolymer, often makes it possible to blend incompatible homopolymers by the use of interpolymerisation reactions, yielding block or graft copolymers in a proportion sufficient to stabilise the dispersion of the system.

The individual segments in block and graft copolymers are joined by primary valence boards, and because these segments can be extended themselves into similar, or the same type of homopolymer, compatibility between a free polymer and a block or graft copolymer can arise. Block and graft copolymers are indeed used almost exclusively in blends that require strong interfacial adhesion.

Systems containing graft copolymers have been prepared by dissolving a rubber in the monomer of a glassy polymer and then polymerising the solution in bulk, preferably with efficient agitation.[5,6]

This method may be varied by the addition of an inert solvent which will improve temperature control and minimise viscosity build up. Another way is to suspend the rubber-monomer solution, often already carried to partial conversion, in a watery phase and to complete the polymerisation as an ordinary suspension polymerisation.[7,8] It has been found that in order to obtain appreciable grafting the dissolved polymer should have a high degree of unsaturation or analogous activity.

Emulsion "overcoat" polymerisation, in which a monomer has been added, for example to a rubber latex, has also been used to produce graft copolymers.[9,10] Provided there is no excess emulsifier graft copolymerisation should take place preponderently but it is doubtful whether grafting is ever achieved to this extent by standard production techniques. Such grafting procedures generally result in systems containing ungrafted rubber, a rubber-on-polymer graft and pure polymer. This situation has been shown to be the case for commercial ABS plastics.[11]

1:3 THERMODYNAMIC CONSIDERATIONS.

A detailed thermodynamic treatment of polymer solubility in low molecular weigth compounds is given in chapter 2. The work on polymer solubility can be traced back to the theory of ideal solutions. The theory was modified to accommodate real solutions, and this in turn has been extended to include polymer solubility and the mixing of solid polymers.

For mixtures of polymers the Gibbs free energy equation

$$\Delta F_M = \Delta H_M - T\Delta S_M \text{----------} (1)$$

Still applies,

where ΔF_M is the free energy of mixing
ΔH_M is the heat of mixing
ΔS_M is the entropy of mixing
T is the absolute temperature.

For the components of a polymer blend to be homogeneously compatible the free energy of mixing must be negative or zero. If it is positive a two phase system will result.

The entropy change for a mixing process is always positive since mixing increases the randomness or disorder of the system. The entropy change depends on the number of molecules per unit volume which decreases with an increase in molecular size. For polymers, the entropy of mixing will be several orders of magnitude less than that for mixing equivalent masses of low molecular weight material.[12]

Thus the sign of ΔF_M will be strongly affected by the heat of mixing term which remains approximately the same with increasing molecular weight. It is a function of the number of molecular unit contacts which remains nearly constant with increase in molecular size. The heat of mixing term is a measure of the affinity of the molecular segments for their environment. A negative value indicates that heat is evolved during mixing, i.e. the two kinds of segments attract the other more than they attract their own kind. If ΔH_M is positive mixing will only occur if it is less than, or equal to the entropy of mixing multiplied by T. A situation where ΔF_M is negative is exceedingly rare in the case of polymer mixtures, the respective molecular segments almost invariably preferring their own environment.[13]

Flory,[14,15,] proposed methods for calculating ΔF_M from theoretical considerations and found it to be positive in all normal cases. Mixing will generally be an endothermic process and polymer blends will generally be incompatible.

Exceptions may arise when there are strong interactions such as polar associations or hydrogen bonding associated with fortuitous molecular geometries. These conditions provide for more favourable association energies which may give rise to compatible polymer blends. The effect of hydrogen bonding has been demonstrated by Smith and coworkers.[16] They found that on mixing aqueous solutions of polyacrylic acid and polyethylene oxide a precipitate was formed which had properties intelligible in terms of molecular compatibility.
Other pairs of polymers containing similar ether and carboxylic acid groups were also found to exhibit similar phenomena. The evidence supporting complex formation through co-operative hydrogen bonding is convincing e.g. the polymeric precipitate may be insoluble in water, forming clear flexible homogeneous films and having a high degree of ordering, indicated by X-Rays.

If thermodynamic theories are to be applied to two phase polymer systems a quantitative means of predicting polymer compatibility in terms of easily measured properties of the polymer is desired. One possibility is through the use of the solubility parameter, δ , which has proved useful in the study of polymer swelling and solubility in low molecular weight liquids.

For a pair of non polar liquids the internal energy change upon solution is given by,

$$\Delta E = \Phi_1 \Phi_2 \ (\delta_1 - \delta_2)^2 \text{ joules/cc of solution}\text{-------}(2)$$

where Φ's are the volume fractions of the components. If amorphous polymers are considered to be essentially liquids, and assuming that the volume change on mixing is negligible, equation (2) is an expression for the heat of solution since

$$\Delta H = \Delta E\text{------------}(3)$$

for constant volume, constant pressure processes.

This equation, combined with equation (2) always gives a positive ΔH indicating that for non polar high polymers true solution will not occur unless the solubility parameters are almost perfectly matched since the $T\Delta S$ term is always small.

Bohn[17] has reviewed the literature on polymer blends and has listed pairs of polymers in tables under the headings compatible or incompatible respectively. He lists 13 compatible pairs and 46 incompatible pairs, but stresses that the compatibility or lack of it, is only considered to be established within the limits given in the tables. Also given in the tables are crude characterisations of the polarity of the two polymers and the differences in their solubility parameters.[18]

Bohn attempted to draw broader conclusions about the criteria necessary for polymer pairs to be compatible. He noted that, although the difference in the solubility parameters, $\Delta\delta$, for compatible pairs was small, there were many examples of incompatible pairs for which this was also true.

He questioned the validity of using values of the solubility parameters which have been determined indirectly from solubility data. It has been suggested[19] that more work should be carried out to determine the compatibility of polymer pairs as an exercise separate from the extensive studies made on polymer-polymer-solvent systems.

Compatible polymer pairs were listed as either both polar or both non-polar, but this was also the case for some incompatible pairs. It was noted that, in the case of polar partners, the polarity must be nearly the same to ensure molecular mixing, estimated in terms of the nature of the polar grouping and its dipole moment.

All the compatible systems involved non-crystalline polymers but Bohn did not consider this surprising since situations involving heats of crystallisation must usually be strongly adverse in respect of molecular mixing. Practical evidence in the literature of compatible pairs involving crystalline polymers is lacking.

Thermodynamic considerations therefore predict that the majority of polymer pairs will be incompatible and their blends will have two phase heterogeneous structures.

1:4 THE NATURE OF BLENDED SYSTEMS.

Before discussing the methods which have been used to determine polymer compatibility it is useful to consider the question of polymer compatibility from thermodynamic considerations and what actually takes place on molecular and macromolecular scales when two high polymers are mixed.

The thermodynamics of mixing indicate that there are three possible types of blended system.

The first is where the components of the blend are completely compatible thermodynamically. Fluctuations in composition of the blends are such that only electron microscopy can show that there may be variations over very small distances. All other test methods indicate that the blend has a homogeneous one phase structure.

As the dimensions of the fluctuations in a blend increase a stage is reached where the components will be very near to the limits of thermodynamic compatibility, being almost completely compatible. If any of the test methods indicate that the components exhibit the properties of a two phase system then they are incompatible. The results obtained from the various test methods, such as low angle X-ray or light scattering, depends on their sensitivity with respect to the blend being studied and no rules can be made.

The third situation is where the components of the blend are thermodynamically incompatible so that a definite two-phase system is formed. Many test methods will indicate that the blend consists of separate phases associated with interfaces and sizeable dimensions.

It has already been indicated that many successful commercial polymer blends have definite two phase structure and some have been shown to be multiphase in character.

When polymer molecules are mixed, even with the application of heat and mechanical work, it is difficult to imagine the molecules diffusing through the melt. Short distance interpenetration involving segments of polymer chains is conceivable but long distance migration of whole molecules through the matrix within the duration of the mixing process is highly improbable. The mixing equipment for polymer blends is large compared with the size of molecules so it is improbable that individual molecules are actually being disentangled during mixing. More likely, the volume elements in the blend which are being mixed involve clusters of molecules containing many chains.[20] Eventually mixing will reach an equilibrium state at which further mixing in the given equipment will not reduce the heterogeneity of the system. It is at this point that we need to consider the structure of the blend completely. It could be a heterogeneous blend with a two phase structure, or the polymers may be compatible enough, and sufficiently disperse, to give a blend which in many respects appears to have a one phase homogeneous structure. It has been shown, and this will be discussed later that, although mechanical tests may show a blend to have a one phase homogeneous structure, such a situation is not decisive of a truly single phase situation.

1:5 METHODS USED TO DETERMINE POLYMER COMPATIBILITY.

The methods which have been used to determine polymer blend compatibility include (a) homogeneity of a solution containing two or more polymers; (b) clarity of a film cast from a homogeneous solution of a polymer blend; (c) dynamic mechanical measurements; (d) measuring the Tg of the blend where Tg is the glass transition temperature; (e) changes in the refractive index with temperature and (f) optical and electron microscopy.

It is usually required that polymer compatibility be evidenced by at least two methods.

If the compatibility of a polymer pair is determined by their ability to form a homogeneous solution in a common solvent then phase separation means that they are incompatible. The classic experiments of Dobry and Boyer-Kawenoki[21] showed that, even in dilute solutions compatible pairs were a rare occurance. Of the 35 pairs of polymers examined only four were found to be compatible. The results were represented in the now familiar triangular diagrams. From their results they made the following observations; (i) Compatibility is the exception and incompatibility the rule (ii) when two high polymers are incompatible in one solvent they are generally incompatible in other solvents (iii) the limits of phase separation depends on the nature of the solvent (iv) the higher the molecular weight, the less compatible are the two polymers and more is the limit of phase separation shifted towards smaller concentrations;

(v) similarity of the principal chain is not sufficient to ensure the miscibility of the polymers (vi) branched chain molecules do not have the same separation limits as linear molecules.

Kern and Slocombe[13] have examined a further 21 pairs of polymers using Dobry's method but found only three compatible pairs, two of which had almost identical structures. Other workers[22-24] have studied polymer-polymer-solvent systems and have found that their results and conclusions agree with those of Dobry.

Films are frequently cast from dilute homogeneous solutions of two polymers in a common solvent to further test the compatibility. An opaque and crumbly film indicates incompatibility and a clear self supporting film suggests better compatibility. Since there is a continuous change in clarity and opacity the transition from a crumbly to a self supporting state is also gradual and it is difficult to judge where compatibility leaves off and incompatibility begins. Whereas translucency or complete opacity is a sure sign that more than one phase is present one may not simply conclude that transparent films means a homogeneous blend. There are cases where heterogeneous blends can give rise to clear films. If the films are very thin, regardless of the dispersed phase particle size, enough light encounters only one of the two phases in passing through the material. Blends in which the particle size is small with respect to the wavelength of the light, such as block copolymers of styrene and acrylonitrile[25] also give clear films.

The same is true in two phase systems in which the indices of refraction of the individual phases are very close, as in the case with poly acrylate-polymethacrylate blends.[26]

Petersen and coworkers[27] have used these first two criteria to study the compatibility of polymer blends. They decided further work was worthwhile because of the growth in the number of new homo and copolymers which had not been studied in solubility tests. They wanted to produce an ultrathin polymeric membrane from a fully compatible polymer blend for use in hemodialysis.

They used twenty different commercial homo and copolymers which, with the exception of polystyrene, all contained rather polar groups. Of over 150 polymer pairs studied only fourteen were compatible, and seven of these contained nitrocellulose. They thought that the results implied that nitrocellulose experienced a negative enthalpy of mixing towards other polymers. The remaining pairs of compatible polymers were heavily dominated by non-crystalline rubbery homopolymers and copolymers. Polymers that had tendencies towards crystallisation were incompatible with all other polymers with which they were paired, confirming the observations of Bohn.[17]

Dynamic mechanical measurements, determinations of glass transition temperatures and measurements of change in refractive index with temperature are methods which have been used, either individually or collectively to determine polymer blend compatibility.

Dynamic mechanical testing has been used intensively by Nielson[28,29] and Takayangi.[30] Basically it consists of subjecting a sample to an oscillating stress (or strain) and measuring the resulting strain (or stress) as a function of frequency and/or temperature. Two fundamental quantities are obtained from these tests, a storage modulus and a loss modulus or damping decrement. The former is a measure of the applied energy which is elastically stored in the material and is related to the tensile modulus. The latter is a measure of the amount of applied energy which is dissipated i.e. converted to heat. When the damping curve for a polymer blend is compared with those for the blends components, a compatible blend will show a maximum between those of the parent polymers. Incompatible polymer blends give two damping maxima corresponding to those of the parent components.

A useful method for determining polymer blend compatibility is to determine the glass transition temperature of the blend. The glass transition temperature is a measure of the segmental mobility of a polymer, and as such it is sensitive to the environment of the segments. In the glassy state large scale molecular motion does not occur, rather atoms and groups of atoms move against the local restraints of secondary bond forces. The glass transition temperature corresponds to the onset of "liquid like motion" of much larger segments of molecules and is characteristic of the rubbery state. If a polymer blend shows two distinct transitions, corresponding to those of the parent polymers, the components are incompatible. A single transition, between those of the components of the blend, shows that the polymers are compatible.

Normally, however, one does not get either a single sharp transition or two transitions. These represent extreme situations with the real results falling between the two. There are several methods for determining glass transition temperatures and these include dielectric relaxation,[31] nuclear resonance[32] differential scanning calorimetry and differential thermal analysis[33] and mechanical testing.[34]

Measuring the index of refraction of a polymer blend is another useful method for studying polymer blend compatibility. If the refracture index is measured over a range of temperatures it is possible to determine the glass transition temperature of the blend. The theory and instrumentation are well discussed in books[35] which also give tables of refractive indices for the common polymers.

The instruments which are used to measure refractive index can be divided into three types, the Abbe, Pulfrich and dipping refractometers. The Abbe refractometer is suitable for measuring the refractive index of solutions but difficulties arise with solids which are in the form of thin films. The problem is that it is difficult to mount the specimens although several modifications have been made to try and overcome this. The Pulfrich refractometer overcomes this problem by mounting the film directly onto the mounting prism. The dipping refractometer is used to determine the refractive index between a standard and an unknown. All three refractometers are fitted with temperature controllers so that accurate measurements can be made at a standard temperature, or over a range of temperatures.

Incompatible blends show two indices of refraction and two glass transition temperatures, compatible blends show one index of refraction and one glass transition temperature. If a blend shows only one index of refraction but two glass transition temperatures the components are incompatible. Either the dispersed phase particle size is so small that light scattering does not occur or the refractive indices of the two polymers are almost identical.

Jenkel[36] has described the use of refractive index-temperature relationships to determine polymer blend compatibility. From the results he was also able to determine the glass transition temperature of the blend which he used as a second test for compatibility. Solid polymer blends were prepared from dilute chloroform solutions. Blends of polystyrene and styrene-methyl methacrylate copolymers gave films which were cloudy and coarsely dispersed. The glass transition temperatures and indices of refraction determined for these blends corresponded to those of the individual components, indicating incompatibility. Blends of polymethyl methacrylate and polyvinyl acetate on the other hand, gave clear films with a single index of refraction. However the blends showed two glass transition temperatures corresponding to the individual components indicating a two phase system. As this was confirmed by dynamic mechanical measurements the dispersed phase particle size must have been such that light scattering did not occur.

Bartenev[37] has determined the glass transition temperatures of mill mixtures of natural rubber and Russian SKB by plotting specific volume as a function of temperature. The glass transition temperature changed in a way that suggested a continually altering molecular environment, something which could only be achieved if the polymers were compatible.

The best known example of a compatible polymer blend is the polyvinylchloride-butadiene/acrylonitrile (NBR) system in which the compatibility is due to the strong interaction between the polar chloride and nitrile groups. Nielsen[28] reported that these polymers were mutually soluble and that a technical mixture gave a single broad transition in a dynamic mechanical test. Wolff[38] and Takayangi[33] have produced compatible blends to support Nielsen's findings. Even so, conflicting evidence indicates that true solubility is only attained over limited ranges of molecular weight and rubber copolymer composition.[39,40]

Wolff and coworkers[41] have reported another system which shows partial compatibility. Blends of polyvinyl acetate with a vinylchloride/vinylacetate copolymer containing 5-10% vinyl acetate were prepared on a two roll mill. Dynamic mechanical measurements indicated that blends with ratios 60/40 and 20/80 were compatible as only one damping maximum was observed. At intermediate ratios two peaks were observed but these did not correspond to the original components of the mixture. They explained these results in terms of a homogeneity gap for intermediate compositions.

Stoelting and coworkers[42] found that blends of poly(2,6 dimethyl - 1,4 phenylene ether) with atactic polystyrene gave two peaks in dynamic mechanical measurements corresponding to the parent polymers and indicating that the polymers were incompatible. When the glass transition temperature was measured by differential scanning calorimetry only one peak was observed which indicated that the polymers were compatible.

The experimental techniques described so far confirm that polymer blends are thermodynamically compatible, incompatible or on the limits of compatibility. Blends which are thermodynamically compatible or incompatible exhibit the properties of a one phase homogeneous system or a two phase heterogeneous system respectively. For blends on the limits of thermodynamic compatibility the results depend on the domain size and the sensitivity of the test method. If the components of a blend will not mix down to small sizes, and one of the test methods indicates a two phase system, they are incompatible. All the test methods described so far indicate that some polymer blends exhibit properties of a compatible mixture with a single phase homogeneous structure.

Optical and electron microscopy, which have proved to be invaluable in studying the structure of polymer blends, have shown that all blends have two phase heterogeneous structures. The principles of optical and electron microscopy are well described in books[43,44] and in the literature[45,46] and will not be discussed here.

Both forms of microscopy are used to determine the dispersed phase particle size of polymer blends, and also to determine which polymer forms the dispersed phase from refractive index measurements. If the refractive indices of the two polymers are almost identical staining techniques can be used to show the two phases. A phase contrast microscope has a lower limit of about 1.0μ but modern electron microscopes can now go down to a few angstroms, which is much smaller than the domain size of polymer blends.

Several different techniques have been used by workers using electron microscopy to study two phase polymer systems. Kato[47] has used osmium tetroxide staining techniques to study ABS plastics. A similar technique has been used by Matsuo[48] to study ABS plastics, high impact polystyrene and P.V.C.-rubber blends. A replica technique has been used by Rovatti and Bobalek[39] to study P.V.C. - butadiene/acrylonitrile copolymer blends which were prepared with and without talc fillers. Gesner[49] has used acetone dispersions to study A.B.S.resins. Kato has also used the osmium tetroxide staining technique to study ABS plastics using optical microscopy. Turley[50] has used optical microscopy to study rubber reinforcement and Traylor[51] has developed techniques to study polystyrene type polymers under phase contract microscopy.

Of the methods discussed, dynamic mechanical measurements, glass transition temperature measurements and optical and electron microscopy give the most useful information on the compatibility of polymer blends.

Thermodynamic predictions and experimental observations show that when polymers of different chemical composition are mixed they will not intermix down to the molecular level. Although blends may show the properties of homogeneous blends in all other tests microscopy shows them to have two phase heterogeneous structures. Polymer compatibility can therefore be considered as a measure of the attractions of two polymers for each other, the greater the attraction the smaller will be the domain sizes of the blend. While polymer compatibility is important, it is not the only factor affecting the success of a polymer blend. There are many polymer blends which rely on a definite two phase structure for their success.

1:6 THE DEVELOPMENT OF TWO PHASE POLYMER SYSTEMS.

Two phase polymer systems have become increasingly important over the last fifteen years. One of the major factors contributing to this has been the development of the rubber reinforced family of polystyrenes. A review of the literature reveals the vast amount of work that has been published on these systems compared with other polymer blends. The aim of the work was to improve the impact properties of styrene polymers without greatly affecting the good characteristics they already possessed. The main developments and theories are summarised below and show that there is scope for some of the successful ideas to be extended to other systems, especially with the number of new polymers which have been introduced in recent years.

The future of polystyrene as a commercial polymer was still in the balance in the early 1940's.[52] It was recognised as a potentially useful polymer because of its good appearance, stability, processibility and low cost but development was hampered by its poor impact properties. Attempts were made to improve the impact strength by increasing the molecular weight, the use of fillers and the deliberate orientation of the polymer molecules but these produced only marginal improvements. Plasticisers were also tried but these had far too severe an effect on the softening point to be of any commercial use.

A break-through came with the introduction of the styrene- butadiene copolymers. These extended the usefulness of polystyrene but were only partially successful in increasing the impact strength. It was not until the advent of the SBR rubber-polystyrene blends, which transformed polystyrene into a tough, yet stiff material, that impact resistant polystyrenes became important commercially.

Polystyrene and rubber can be blended in a number of ways. Originally the polymers were compounded on a two roll mill, in internal mixers or in extruders but the impact strength of the resultant blends were variable, and little better than that of unmodified polystyrene. Blending styrene-butadiene latex with polystyrene latex, followed by coagulation and drying has also been used but again the improvement was only marginal.

Today the common practice is to dissolve the rubber in styrene monomer and then polymerise the styrene in the usual way.

The resultant blend contains copolymer in which short polystyrene side chains are attached to a rubber backbone, as well as SBR and polystyrene homopolymer. This method was found to give the improvement in impact strength required by manufacturers to extend the usefulness of polystyrene.

The development of the ABS plastics has been on similar lines to that for the impact polystyrenes. Several methods of preparation were tried before a blend with the desired properties was produced. The mechanical mixing or latex blending of styrene/acrylonitrile copolymers with butadiene/acrylonitrile copolymers produced blends which showed little improvement in impact strength because of the partial compatibility of the two copolymers. The desired improvement in the impact strength was finally obtained by overcoat polymensation in emulsion of polybutadiene dispersions in water specially prepared with particle sizes in the region of 0. 5 μ.

The main interest in two phase systems is the ability of the dispersed particles of the rubbery phase to improve the impact strength of the glassy matrix. The impact strength in this case is defined as the ability to withstand a shock loading without undergoing brittle failure.

The rubbers used in two phase impact systems have a high impact strength and a low modulus while the blends themselves have a modulus which is slightly lower than the glassy component alone, and a yield point below the ultimate tensile strength of the glass.

After the yield point the blend shows ductile deformation, during which whitening occurs, up to the point of failure.

In an early attempt to explain the impact properties of rubber reinforced polystyrene Merz, Claver and Baer[53] attributed the impact strength to the energy absorbing properties of the dispersed rubbery phase and postulated that most of the applied energy was absorbed by the particles. They pictured the rubber particles holding together the fracture surfaces of the continuous glassy phase beyond the yield point of the composite, thus preventing a crack passing through it, which would lead to failure.

Strella and Newman[54] have shown that this mechanism cannot explain the improved impact strength because the amount of energy which can be absorbed by the rubber particles at the point of failure is only a small fraction of the amount of energy actually absorbed. It should be noted, however, that the mechanism proposed by Merz required that there was good adhesion between the glassy and rubbery phases.

Several workers have considered the effect of crackformation. Schmitt and Keskkula[55] have taken photographs which show that when a rubber modified polystyrene is strained microcracks are formed radiating from the rubber particles. Staverman[56] using a similar system, took photographs which suggested that the propogating cracks were diverted by the rubbery particles, passing between, rather than through them. Both groups of workers felt that the formation of a multiplicity of microcracks in the glassy phase could dissipate enough energy to account for the improved impact strength. More recent work has, however, indicated that microcrack formation is not the major energy absorption mechanism in two phase impact systems.

Howard and Mann[57] and Strella and Newman[54] have shown that, in a two phase system which has been stretched beyond its yield point, essentially all of the deformation can be recovered by heating the material above the Tg of the continuous glassy phase. The deformation is due to the molecular orientation of the glassy phase and photographic evidence for this drawing in the neighbourhood of the rubber particles has been presented.[57,58].

Since such molecular orientation cannot take place below a polymer's Tg, particularly at the loading rates involved one, or both of two things must be occurring. Either there is localised heating of the glassy phase and/or a decrease in the Tg of the glassy phase. It has been suggested that the rubbery inclusions may act as stress concentrators, providing sufficient local working to raise the temperature enough to initiate drawing. Dynamic mechanical data indicates that, under shock loading conditions, a relatively large proportion of the energy applied is converted to heat which may contribute to raising the local temperature. Strella and Newman[54] discuss in detail the fact that a tensile stress on a material whose Poisson's ratio is less than 0.5 results in an increase in free volume, and that increasing the free volume of a polymer decreases its Tg. In two phase impact systems the glassy phase has a Poisson's ratio of less than 0.5 (often about 0.35), while that of the rubbery phase is about 0.5. If the rubbery and glassy phases are bound strongly enough at the particle interface to prevent separation and void formation, the rubber will tend to prevent the expansion of the surrounding glassy material, putting it under additional stress and further lowering the Tg.

They show, with appropriate calculations that this mechanism can result in the initiation of drawing in the region adjacent to the rubber particles.

Support for this theory has come from Bucknall and Smith.[59] They have presented photographic evidence for impact polystyrenes which shows that what had previously been considered to be microcracks were in fact crazes. These crazes, which are areas of highly orientated polymer interspersed by voids, are the same as those observed when untoughened polystyrene is strained. The presence of the rubbery particles shortens the individual crazes and greatly increases their number, and this in turn increases the fraction of glassy material converted to crazes. Thus, the high elongation and energy absorption in two phase impact polymers results from the drawing of the glassy phase to form a high percentage of crazed material. The familiar stress whitening which occurs is due to the difference in the refractive index of the orientated craze areas and the unorientated glass.

The present concept of rubber reinforcement requires that the rubber particles be large enough to start and stop craze development, exhibiting typical rubbery properties with adhesion between the rubbery and glassy phases. This indicates the need for a minimum dispersed phase particle size which has been shown to be of the order of 0.1 to 1 microns for effective reinforcement, depending on the character of the glassy matrix. If the heterogeneity is reduced to molecular levels, as is the case with ordinary copolymers, or the affinity of the components is such that they are mutually soluble, the result it plasticisation and not an improvement in impact properties.

To obtain a successful two phase impact plastic an optimum compatibility between the phases must be achieved, great enough to provide the necessary adhesion at the rubber-glass interface, yet not so great that the discrete two phase character is destroyed by solubility.

It was found that the most successful method for improving adhesion was to graft the glassy monomer onto the rubber backbone. The grafted side chain is quite compatible with the surrounding glassy phase, and is chemically bound to the rubber resulting in excellent adhesion. Bevilacqua[60] and Howard and Mann[57] have obtained electron micrographs of rubber latex particles covered by "lumps" of grafted glassy polymer..

Dynamic mechanical measurements can be used to distinguish between blends which do, or do not exhibit good impact properties. Styrene-butadiene copolymers and compatible blends of SBR and polystyrene, whose impact strength is only marginally better than polystyrene, exhibit one damping maxima which is intermediate between those of pure glass and the rubber. On the other hand, blends with good impact properties show two damping maxima, corresponding to the original components of the blend.

Good impact strength in two phase systems also requires that the Tg of the rubbery component be well below (about 40-50°C) its use temperature. Thus good low temperature impact properties require the use of a rubber with a low Tg.

Experiments on the toughening of polystyrene has not been restricted to styrene-butadiene rubbers. It is claimed[61,62] that a stereo regular cis 1-4 polybutadience is more effective in toughening polystyrene than SBR. The reasons for this greater effectiveness include a better balance of the compatibility factors, the lower Tg of the rubber (-100 instead of -55 for SBR), its greater resilience and its higher reactivity towards grafting.

Another interesting observation is that homopolymers noted for their good impact strength such as nylons, cellulose acetate, polyethylene and polycarbonate exhibit dynamic mechanical responses similar to those fortwo phase impact plastics. Bobalek and Evens[63] showed that the fracture surfaces of these materials had a heterogeneity similar to that observed with two phase impact plastics. They concluded that the requirement for good impact strength is the co-existence of a rigid (whether glassy or crystalline) and rubbery phases.

Until recently, due to the amount of work which has been published on the styrene modified polymers, valuable work on other polymer blends has been overshadowed. Rossen[19] in a review on two phase polymer systems, has considered mainly styrene modified polymers but indicated that he hoped it would stimulate work on other heterogeneous systems. As indicated previously,it was hoped that a process which had proved successful for one system could be extended to others. It was thought that the idea of polymerising a monomer in the presence of a dissolved polymer could easily be extended to other monomers.

1:7 THE AIMS AND SCOPE OF THE THESIS.

Caprolactam, which can readily be polymerised to nylon 6 (polycaprolactam) was considered to be a suitable monomer. Caprolactam is an important commercial monomer, being produced in large quantities on an industrial scale. Several low cost methods for producing it have been developed in the last few years, giving a monomer of high purity in high yields. Caprolactam is usually polymerised to nylon 6 by one of two methods. The first is in an autoclave or continuous reactor using water as the catalyst. The polymer produced by this method is in equilibrium with about 10% monomer which must be removed,at least in part,as it has a pronounced effect on the properties of the final product. Nylon 6 prepared in this way is used to produce tyre cord, textile fibres, filaments and bristles, is used in extrusions and mouldings and is formed into films. Caprolactam can also be polymerised by an anionic mechanism, the reaction being carried out below the melting point of the polymer and at atmospheric pressure. This makes the technique attractive for the production of large cast articles, but small items will continue to be made by extrusion and injection moulding.

Laurolactam, which is starting to become important commercially, was used as a "solvent" in the work on polymer solubility, the results being compared with those for caprolactam. Laurolactam can be polymerised to nylon 12 by an anionic mechanism similar to that for caprolactam.

Caprolactam polymerisation has been well studied by Witcherle and Sebenda[64,65] and other workers[66] and the reaction mechanism is known.[67,68].

Encouragement for the use of caprolactam as a polymerisable monomer is given in the literature. A Du Pont patent[69] describes the use of polycarbonates as cocatalysts in the anionic polymerisation of caprolactam but no reaction mechanism is given and the structure of the polymers obtained is not described. A Russian patent[70] describes the preparation of homogeneous blends of polyamides and polyformaldehyde. Homogeneous mixtures were obtained by dissolving the polyformaldehyde in the polyamide monomer and polymerising the monomer. Matzner and coworkers[71] have described the use of chlorine terminated polysulphone and polysulphone as cocatalysts in the anionic polymerisation of caprolactam at temperatures of 160°C.and above. In both cases block copolymers were produced. One disadvantage in using caprolactam as a monomer is that as yet compatible blends containing a crystalline polymer are unknown. On the other hand the formation of block and graft copolymers could produce useful polymers for use on their own or when blended with other polymers.

The properties of nylon 6 are summarised below but a more detailed description of nylon 6, and the other polyamides is given in books and in the literature.[72] Nylon 6 polymer is characterised by a combination of high strength, elasticity, toughness and abrasion resistance. It is somewhat softer and less stiff than nylon 6,6 because of its lower crystalline melting point but nylon 66 has better heat resistance. The solvent resistance of nylon 6 is good, only phenols, cresols, and formic acid dissolve the polymer at room temperature. Strong acids degrade the polymer and it is also degraded by hydrolysis at elevated temperatures. If the polymer is to be used outdoors, it must be stabilised or pigmented with carbon black as its weatherability is only fair. All nylons readily absorb moisture from the air and the saturation moisture content of nylon 6 is 9-10%.

Water acts as a plasticiser, reducing the modulus and tensile strength but at the same time increasing its elongation. Therefore, although nylon 6 is a good polymer it can be improved and there is evidence of this in the literature.[73,74]

The aim of this work was two fold, to study the solubility of a series of commercial polymers in caprolactam and laurolactam and to prepare polymer blends, and if possible copolymers, by polymerising caprolactam in the presence of dissolved polymers.

It was felt that if a second polymer was to have an effect on the properties of nylon 6 it would easily be seen what they were if it was present to an extent of 10% by weight. Accordingly, the solubility of a series of commercial polymers in caprolactam and laurolactam at 150°C was studied by attempting to dissolve 10% by weight of each polymer in the monomers. It was found that, although the majority of polymers were insoluble or only slightly soluble, some did dissolve. The results were discussed in terms of polymer solubility parameters, hydrogen bonding and polymer crystallisation.

When polymers dissolved to an extent of 10% by weight the monomer was polymerised in the presence of the polymer by an anionic mechanism. It was found that different polymers required different techniques in order that the monomer could be polymerised. If the polymer contained groups which were readily attacked by the cocatalyst the lactam anions had to be formed in a separate reaction vessel. Of the polymers studied, it was found that polycarbonate and polysulphone acted as cocatalysts in the anionic polymerisation of caprolactam, copolymers being formed.

None of the polymers soluble in laurolactam acted as cocatalysts. Polymer blends were formed when the lactam monomers were polymerised in the presence of other polymers.

Polysulphone, one of the newer, heat resistant polymers which acts as a cocatalyst in the anionic polymerisation of caprolactam, was considered to have useful properties which might be beneficial if combined with nylon 6. Polysulphone-polycaprolactam copolymers were prepared in order to determine the copolymer composition, the reaction mechanism and to determine the molecular weight of the polysulphone component of the copolymers. Optical microscopy was used to study the phase structure of the copolymers as the polysulphone concentration was increased. Some of the physical properties of the copolymers were measured and compared with those of a commercial nylon 6.

Polymer blends were prepared by dissolving polystyrene, impact styrene and S.B.S. thermoplastic rubber respectively in caprolactam and polymerising the monomer by an anionic mechanism. The composition of the blends was determined, their phase structure was examined by optical microscopy and some of their physical properties were compared with those of commercial nylon 6 and polycaprolactam homopolymers. It was hoped that the results would be of use in trying to explain why blends with crystalline polymers are incompatible.

2. POLYMER SOLUBILITY.

2:1 INTRODUCTION.

Predictions of the compatibility of polymers with other polymers, or solvents, are usually attempted from thermodynamic considerations, or less precise considerations derived there from.

The driving force of any process in thermodynamic terms is the free energy, and is given by the Gibbs free energy equation, equation (1).

$$\Delta F_M = \Delta H_M - T\Delta S_M \text{ - - - - - - } (1)$$

In the simple case of an ideal solution [75] ΔH_M is, by definition zero. Whether mixing occurs depends on the entropy of the system. The entropy change on mixing can be derived from Raoult's law, or from statistical mechanics such that

$$\Delta S = -R(n_1 \ln N_1 + n_2 \ln N_2) \text{ - - - - - - } (4)$$

where R is the gas constant

n is the number of moles of each component.

N is the mole fraction of each component.

As this expression is always positive spontaneous mixing will occur among ideal systems in all proportions. The implication is that the free energy of mixing must be negative for the production of a thermodynamically stable molecular mixture.

However, few systems are ideal, and the heat of mixing ΔH_M is not equal to zero. Hildebrand[76] gave the name "regular solutions" to the class of liquids in which ΔS_M has nearly the ideal value but ΔH_M is not equal to zero. Since the entropy of mixing is always positive in regular solutions the heat of mixing will critically determine whether or not two substances will mix spontaneously, and the associated limits.

ΔH_M for mixing is a measure of the attraction between the molecules to be mixed. A negative ΔH_M means that heat is evolved during mixing and the molecules will attract each other more than they attract their own kind. If ΔH_M is negative then spontaneous mixing will occur, but if it is positive mixing will only occur under conditions where

$$\Delta H \leqslant T\Delta S$$

A factor affecting polymer solubility is the difference in free volume between the polymer and the solvent. If a polymer is considered to consist of segments connected by stiff covalent bonds that restrict the thermal motion of the segments, the thermal expansion of the polymer will be relatively small, and decreases with an increase in the chain length of the polymer. Dissolving a polymer in a solvent is accompanied by large changes in the free volume by both the polymer and the solvent, the polymer expanding and the solvent contracting to attain the average free energy of solution. The change in the free volume is more important for the solvent so that the net change of volume during mixing corresponds to a contraction. The overall contraction during mixing brings the molecules close together so that mixing is an exothermic process and there is a negative contribution to the heat of mixing. As the contraction also corresponds to a lessening of molecular disorder there is also a negative contribution to the entropy of mixing. In principle these negative contributions to ΔH_M and ΔS_M could cancel out but it is found that the contribution to ΔS_M is more important than that to ΔH_M so that there is a positive contribution to ΔF_M. As the volume of the solvent rapidly increases with temperature relative to that of the polymer, the free volume contribution increases with temperature.

Furthermore, since the solvent is more compressible than the polymer the application of pressure decreases the free volume of the solvent more than that of the polymer and increases polymer solubility.

Patterson[77] has considered the effect of molecular shape and size on polymer solubility. He has suggested that, in addition to the effects mentioned above, there is an effect arising from an ordering of molecules of liquids composed of long chain molecules and certain polymers. Long chain molecular liquids such as n - hexadecane are not distributed completely at random, but, in order to improve packing, the chains run parallel to each other over short distances. Evidence for this ordering comes from measurements of the depolarisation of scattered light from these liquids. As the only molecules considered in this work were alkane isomers of formula C_6H_{14} or $C_{16}H_{34}$ other molecules need to be studied to determine the significance of this effect on polymer solubility.

Four types of interaction are generally considered in solutions of non-electrolytes. These are

(1) Dispersion (London)forces.

(2) Dipole-dipole interactions.

(3) Dipole-induced-dipole ineractions.

(4) Hydrogen bonding.

The change of internal energy, ΔE, needed to overcome such interactions in the case of a simple liquid is related to the molar heat of vapourisation ΔH_V by equation (5)

$$\Delta E = \Delta H_V - RT \text{ - - - - - - } (5)$$

ΔE is known as the molar cohesive energy and is defined as the energy required to break all the molecular contacts in a mole of liquid. If V is the molar volume then equation (5) becomes

$$\frac{\Delta E}{V} = \left[\frac{\Delta H_V - RT}{V}\right] \qquad \text{------- (6)}$$

$\frac{\Delta E}{V}$ is now defined as the cohesive energy density.

Early workers considered only ideal solutions and solutions in which there were only weak interactions. Hildebrand and Scatchard[78] noted that, when only dispersion forces were present, the cohesive energy density of a pair of dissimilar liquids was approximately equal to the geometric mean of the cohesive energy densities of the components. They derived an expression for the heat of mixing using the assumption.

$$H_M = V\phi_1 \phi_2 \left[\left(\frac{E_1}{V_1}\right)^{\frac{1}{2}} - \left(\frac{E_2}{V_2}\right)^{\frac{1}{2}}\right]^2 \qquad \text{------ (7)}$$

Where ϕ is the volume fraction

and V is the total volume of solution.

Hildebrand called the expression $\left(\frac{E}{V}\right)^{\frac{1}{2}}$ the solubility parameter and assigned to is the symbol δ. The solubility parameter is in fact a measure of all the intermolecular forces present.

Equation(7) can now be written as

$$\Delta H_M = V\phi_1\phi_2\left[\delta_1 - \delta_2\right]^2 \qquad \text{-------- (8)}$$

The partial molar heat of mixing is given by

$$\overline{\Delta H}_M = V_1\phi_2^2 \left[\delta_1 - \delta_2\right]^2 \text{-------- (9)}$$

Where V_1 is the molar volume of the solvent

ϕ_2 is volume fraction of the second component

Although equation (9) was derived from solvents and solutes of similar molecular volume, it has been used extensively for predicting polymer solubility by combining it with an entropy term. Flory[79] and Huggins[80] succeeded independently in deriving an expression for the entropy of mixing high polymer solutions by calculating the number of possible configurations for a mixture of polymer and solvent molecules arranged in a lattice. The individual segments of the polymer chain were considered to be similar in size to the molecules of solvent.

The entropy is given by

$$\Delta S = - R (n_1 \ln X_1 - n_2 \ln X_2) \quad \text{- - - - - -(10)}$$

which is similar to equation (4). In equation (10) the volume fraction has replaced the mole fraction.

Flory[81] has extended this work by modifying the heat of mixing term in a way similar to which he modified the entropy of mixing term. By combining the expressions for the partial molar heat of mixing and the partial molar entropy of mixing an expression for the partial molar free energy of mixing of a polymer solution was obtained.

It is known as the Flory-Huggins partial molar free energy equation. In deriving this equation Flory introduced a solvent-solute interation parameter χ. He showed that the solubility of a polymer in a given solvent is controlled by the value of χ as it is a free energy parameter. Flory[82] later suggested that χ should be replaced by a power series in concentration. This treatment, while limited in detail, works reasonably well for non-polar polymers in various non-polar solvents. It was not until the middle sixties that any satisfactory treatments for polar and hydrogen bonding solvents began to appear and these will be considered later.

When it was realised that cohesive energy densities were important in controlling solubility methods for estimating them became important. For non-polymeric materials this was relatively easy as they could be calculated from vapour pressure data (equation 5). Calculating solubility parameters from vapour pressure data has recently been reviewed by Hoy.[83] Using the equations of Huggenmacher[84] and computational methods he has calculated the solubility parameters for a broad range of solvents and chemicals.

Although the vapour pressure method cannot obviously be applied to polymers it was noted that liquids with like solubility parameters were apt to dissolve the same solutes and be mutually compatible. It therefore seemed reasonable to extend this method to studies of polymer solubility. Two experimental methods are quoted in the literature. The first method involves the swelling of a slightly cross-linked analogue of the polymer being studied in a series of solvents. The δ_p value for the polymer is taken as the δ value of the solvent in which it swells most so that the determined value is somewhat dependent on the cross-link density. Gee,[85] and Bristow and Watson[86] have studied the swelling of various rubbers in various solvents. The second method involves measuring the intrinsic viscosity of a polymer in a series of solvents. The value of δ_p is taken as being equal to the δ_s value where the intrinsic viscosity has a maximum. Generally a plot of intrinsic viscosity against solvent solubility parameter gives a bell shaped curve with a reasonably well defined maximum. When discussing the significance of such results the nature of the solvent must be taken into consideration. More or less polar and more or less hydrogen bonding solvents often provide different curves.

In both cases specific interactions and differences in molar volume make the estimation of δ_p more difficult. Both methods have the disadvantage of being laborious and time consuming.

There are several methods for calculating solubility parameters from thermodynamic data.[87] They can be calculated from critical pressure data, from the relationship of pressure and temperature, and also from the Van der Waal's gas constant. There is also a method for estimating solubility parameters at various temperatures but the values are not usually quoted above 30°C. It should be possible to estimate solubility parameters at T°K from the coefficients of thermal expansion α, and the compressibility β by the equation.

$$\delta \approx \left(\frac{\alpha T}{\beta}\right)^{\frac{1}{2}} \quad ------ (11)$$

This equation could provide a means for the direct estimation of δ for polymers because α and β should be measurable. The method is mainly of theoretical interest for liquids since thermal coefficients are not available.

Small[88] has described a method for calculating solubility parameters which does not involve experimentation. Assuming that the geometric mean rule holds, he found that the solubility parameter contributions of different groups in a molecule, to the overall solubility parameter, were additive. He determined a set of additive constants for the commoner groups in organic molecules and from them calculated $(EV)^{\frac{1}{2}}$. He called them molar attraction constants and gave them the symbol F. ΣF summed over the groups present gives the value of $(EV)^{\frac{1}{2}}$ for one mole of substance concerned.

The molar cohesive energy, E, the cohesive energy density C.E.D and the solubility parameter δ are then given by

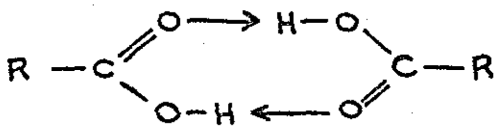
$$E = \frac{(\Sigma F)^2}{V} \quad ; \quad C.E.D. = \frac{(\Sigma F)^2}{V} \quad ; \quad \delta = \frac{\Sigma F}{V} \text{ - - - - -(12)}$$

All compounds in which hydrogen bonding occurs, or which are highly polar, were excluded from this work. Compounds containing hydroxyl groups, nitrogroups, amines, amides and carboxylic acid were among those not considered.

The compounds for which Small's formula did not work were the lower esters and ketones. For these compounds data for higher members of the series were used instead. The results obtained by Small were excellent for olefins and varied from reasonable to good for the other organic compounds considered. Steric effects, conjugation and ring closure are some of the factors which effect the value of F. Packing several large atoms or groups of atoms round a central atom results in the observed value of $(EV)^{\frac{1}{2}}$ being lower than the calculated value. For carbon tetrachloride the value of $(EV)^{\frac{1}{2}}$ by Small's method is 987 $cal^{\frac{1}{2}}$ $cc^{\frac{1}{2}}$ and the observed value is 835. Conjugation in styrene and butadiene and ring closure results in an increase in $(EV)^{\frac{1}{2}}$ over that calculated by Small's method. Small found that the lack of reliable density data for well characterised polymers was a cause of some uncertainty in the calculated value of δ.

Although Small made no attempt to treat compounds in which hydrogen bonding occurs his method has been successfully extended to cover carboxylic acids by Hoy.[83] In many compounds in which hydrogen bonding occurs the experimental values of δ and those obtained in Small's method differ considerably.

If, for carboxylic acids, the calculations are made assuming the acid to exist as a monomer Small's method does not give accurate predictions for the value of δ . Hoy assumed that the acids existed in the dimer form and adjusted the calculations of the solubility parameter accordingly. Using the dimeric structure



and computational analysis Hoy obtained satisfactory results for fourteen carboxylic acids.

The solubility parameters of some types of polymers which do not contain polar or hydrogen bonding groups, such as copolymers or crystalline polymers, may also be difficult to define. The solubility behaviour of random, block and graft copolymers is often quite different and it is therefore not justifiable to assign the same overall cohesive energy density value to such polymers. Partially crystalline, or crystalline polymers have a lower free energy than the corresponding amorphous polymer and in order to dissolve them the free energy necessary to melt the crystals must be supplied. Entropy changes increase on the disordering of molecules and make it easier for polymers to go into solution. However, the amount of energy required may not be compensated for by the entropy gain and in such cases the polymer may go into solution only if heat is supplied. Crystalline polymers much below their melting points are often only appreciably soluble in solvents which have some special interaction with them. Such interactions are usually hydrogen bonding. For crystalline polymers such as polyethylene and polytetrafluoroethylene, in which there is no possibility of hydrogen bonding, the heat requirement for melting the crystals is so high that they are insoluble in all solvents at room temperature.

A crystalline polymer which shows specific interactions is nylon 6 which is soluble in formic acid and phenols at room temperature because it can form hydrogen bonds with them.

The preceding discussion has been concerned with solutions in which only weak forces are involved and the equations derived are only applicable to simple systems. If hydrogen bonding forces are present in a system they are usually strong enough that they cannot be ignored. The strength of a hydrogen bond falls between that of dipole interactions and chemical bonds. Water would be a gas if it were not for hydrogen bonding which causes the molecules to cluster together. Most polar compounds such as alcohols and ketones associate into clusters due to hydrogen bonding. Small discussed the importance of hydrogen bonding and thought that at least two parameters would be required to express the properties of hydrogen bonded liquids. The first is related to the hydrogen bond accepting capability and the second to the hydrogen bond donating ability of the molecule involved. He proposed equation (13) as a measure of the contribution of hydrogen bonding (ΔH_h) to the heat of mixing

$$\Delta H_h = \phi_1 \phi_2 (\sigma_1 - \sigma_2)(\tau_1 - \tau_2) \text{-----}(13)$$

where σ is the hydrogen bonding accepting ability

τ is the hydrogen bonding donating ability

ϕ is the volume fraction.

He suggested that when hydrogen bonds were formed it might be more appropriate to use mole fractions instead of volume fractions. Although parameters such as σ and τ have not been measured equation (13) has been used to make qualitative predicitions of the effect which can be expected for various mixtures.

One of the first practical methods for treating hydrogen bonding forces in solution was devised by Burrell.[89] He classified solvents by their tendency to form hydrogen bonds. His classification is as follows:- (a) Strongly hydrogen bonded (e.g. alcohols, carboxylic acids, water, pyridine), (b) Moderately hydrogen bonded (e.g. ketones, esters, ethers, aniline.), (c) Poorly hydrogen bonded (e.g. hydrocarbons, halogen compounds, nitro compounds, nitriles.)

Liebermann[90] arbitrarily assigned number ranges to Burrell's classification and then determined an empirical hydrogen bonding number for each solvent from solution data. He then portrayed polymer solubility on a plot of hydrogen bonding number versus solubility parameter. These were the first in a series of papers by different authors who have tried to treat polar and hydrogen bonding solutions thermodynamically.

Blanks and Plausnitz[91] have given a detailed treatment of polar solvents in which the solubility parameter is split into two parts. One is associated with normal Van der Waals forces (dispersion forces) and the other is associated with polar forces.

Crowley, Teague and Lowe[92,93] have used three dimensional plots for displaying polymer phase diagrams, volumes of solubility being drawn up for a number of resin types from existing data. The three parameters chosen relate to the three types of intermolecular forces that occur. These are dispersion, polar and hydrogen bonding forces represented as follows:

δ - the classical Hildebrand solubility parameter.

γ - a measure of hydrogen bonding obtained by the spectroscopic technique of Gordy and Stanford.

μ - dipole moment, as a measure of dipole-dipole interaction.

Hansen[95-97] has done work on similar lines to that of Crowley. He has split the Hildebrand solubility parameter into three parts on the assumption that it is a measure of all three types of intermolecular force. The three components are dispersion, polar and hydrogen bonding forces and are represented by :-

δ_d - which describes the dispersion forces.

δ_p - which describes the dipole-dipole and dipole-induced-dipole interactions.

δ_h - which describes the hydrogen bonding forces.

Hansen obtained an equation for δ on the assumption that the total energy of vapourisation was an additive quantity such that

$$E^v = E^v_d + E^v_p + E^v_h \text{ ------ } (14)$$

dividing through by the molar volume gives

$$\delta^2 = \delta^2_d + \delta^2_p + \delta^2_h \text{ ---- } (15)$$

Using these solubility parameters Hansen constructed a three dimensional solubility diagram. A polymer is represented by a point round which a sphere can be constructed. Any liquid characterised by a point lying within the sphere is a solvent for the polymer while a liquid represented by a point outside the sphere is a non-solvent for the polymer. The radius of the sphere must be determined experimentally. By using this approach a suitable solvent for a polymer can be chosen without laborious experimental work. It is also more powerful than Flory's interaction parameter for characterising solvent power.

One of the advantages of this approach is that it avoided the arbitrary axes which were used by Crowley. Although Hansen was able to obtain an equation for δ he was unable to solve is completely.

By using the homomorph concept introduced by Blanks and Plausnitz[91] he was able to determine the value of δ_d^2. This left $(\delta_p^2 + \delta_h^2)$ which he referred to as δ_v^2, but was only able to solve it empirically. Although his approach has been very successful Hansen realised that many problems remained. The homomorph approach failed in the case of solvents containing chlorine and sulphur atoms and in other cases the proper homomorphs were hard to choose. The effect of temperature on the solvent parameters was also unknown. For larger molecules where the total energy of vapourisation was not available the solubility parameter has to be calculated by Small's method.

Bagley, Nelson and Scigliano[98] have considered solubility parameters and their relationship to internal pressure measurements in polar and hydrogen bonding solvents. By making precise internal pressure measurements they were able to make determinations of the characteristics of a solvent and the effect of temperature on them. They did this by considering two solubility parameters, the first a volume solubility parameter and the second a residual solubility parameter. These can be related to Hansen's three dimensional solubility parameters

$$\delta_v = \sqrt{P_i} \equiv (\delta_d^2 + \delta_p^2) \qquad \text{------} \ (16)$$

$$\delta_r = \delta_h$$

where δ_v is the volume solubility parameter

δ_r is the residual solubility parameter

P_i is the internal pressure.

Bagley thought it possible that only two solubility parameters were needed to describe δ for a solvent. One corresponds to the "physical" contribution (polar and non polar effects) and the other to the "chemical" contribution (hydrogen bonding effects).

Bagley and Chen[99] have studied hydrogen bonding effects in solution using the two dimensional solubility parameter. Chen[100] has extended this study to treat Polymer/solvent and polymer/plasticiser systems. The solvent power of an organic liquid was considered to be characterised by the parameters δ_h and χ_H. δ_h is the hydrogen bonding solubility parameter of the liquid and χ_H is the term which takes into account the dispersion and polar interactions between the liquid and the polymer and also the effects due to temperature. Chen showedthat Hansen's solubility sphere can be represented by a solubility circle in an $\chi_H - \delta_h$ plane. He used Hansen's solubility data and experimental and calculated values of δ_d, δ_p and δ_h for the liquids and polymers considered. He derived an expression for χ such that

$$\chi_H = \frac{V_L}{RT}\left[\left(\delta_{d_L} - \delta_{d_P}\right)^2 + \left(\delta_{p_L} - \delta_{p_P}\right)^2\right] \text{- - - - - - - -} (17)$$

which he solved using Hansen's data.

The solubility circle for a given polymer was determined by first locating the polymer, and all the liquids considered in the $\chi_H - \delta_h$ plane and then determining the solvent power of a few liquids at different distances from the polymer. Hansen classified polymer/liquid mixtures into six groups and Chen, assigning a different symbol for each group used it when plotting his graphs. The smallest polymer-non solvent distance is the radius of the solubility circle for the polymer. Solvents which lie within the circle should be solvents for the polymer.

The best solvents for a polymer should be represented by points close to the centre of the circle.

Solution thermodynamics indicate that large χ_H values, or a large difference in the δ_h values of polymers and liquids, favours immiscibility in a polymer solution. Self association of the solvent or polymer in a polymer solution favours immiscibility while mutual association between polymer and solvent favours miscibility.

The use of such a two dimensional solubility parameter means that the contribution of hydrogen bonding to the heat of mixing can be separated from the physical contribution in all kinds of mixtures. The work also showed that the dispersion and polar contributions have a similar nature which is indicated by equation (17).

Chen only considered three polymers and suggested that a more precise relative scale between the δ_h and χ_H axes could be obtained by extending the work to cover more polymers. This work could also be extended to polymer solubility in mixed liquids and to polymer-polymer compatibility in blends.

Nelson, Hemwall and Edwards[101] have looked at the methods for predicting solubility and concluded that, in the cases of solvents capable of hydrogen bonding they were inadequate. Methods for estimating hydrogen bonding forces in solution usually considered them to act in the same way as polar and dispersion forces.

When dispersion and polar forces are the only forces acting in a system their contribution to the heat of mixing is either zero or positive. Hydrogen bonding forces can however, make a positive or negative contribution to the heat of mixing.

By using Small's equation (equation 10) as a measure of the contribution of hydrogen bonding forces to the heat of mixing it is possible to predict the effects which can be expected for various mixtures. The most favourable situation for miscibility is when a compound which can act as a proton donor is mixed with one that can act as a proton acceptor. In this case the contribution to the heat of mixing is negative which enhances solubility. Unfavourable contributions to the heat of mixing occur in systems containing donor/acceptor molecules. This is because some of the inter-molecular hydrogen bonds which exist in donor/acceptor systems must be broken if that compound is to exist in a single phase with another compound.

Any explanation for the effects of hydrogen bonding on solution properties must therefore take into consideration both the positive and negative contributions to the heat of mixing. Nelson has proposed a hydrogen bonding parameter, referred to as a "net hydrogen bonding accepting index" θ_A which is given by equation (18)

$$\theta_A = \sum_{i=1}^{n} k_i V_i \gamma_i \quad ------ \quad (18)$$

where V_i is the volume fraction of the i^{th} component of the blend

γ_i is its hydrogen bonding parameter.

k is a weighting factor.

Nelson has pointed out that equation (18) is not an attempt to define hydrogen bonding interactions in rigorous thermodynamic terms. Rather it is an improved method for predicting relative effects due to hydrogen bonding interactions because it recognises unfavourable contributions of the heat of mixing. It also helps to explain why solvents which are predicted to be similar by other methods, do in practice differ widely in their ability to dissolve particular polymers.

Nelson also points out that the popular methods for solvent selection are based on the theory of regular solutions. In a regular solution there are no strong associations between molecules so the entropy of mixing is nearly ideal. This is probably a good approximation when only polar and dispersion forces are involved but not so when hydrogen bonding forces are involved. Hydrogen bonding forces can be quite strong,and substantial association between molecules can occur in hydrogen bonding mixtures so that the entropy of mixing is far from ideal. Therefore, although polar and dispersion forces are usually adequately described by heat of mixing parameters related to solubility, more is required when hydrogen bonding forces are involved. He has suggested that the hydrogen bonding parameter should be a free energy parameter to account for the entropy deviations caused by hydrogen bonding.

Although much progress has been made in the last ten years in assessing the fundamental factors concerned with polymer solubility much has still to be done. As yet no thermodynamic theory can treat situations quantitatively, nor is it able to handle precisely the effects of polymer concentration. The behaviour of two polymers in a common solvent cannot be predicted from existing theory either.

In view of the importance of solubility and compatibility in polymer solutions Rudin and Johnson[102] have suggested a completely different approach. They have suggested that a model based on kinetic rather than thermodynamic considerations might give results in better agreement with experimental observations. The polymer/solvent mixture is treated as a colloidal dispersion that may coagulate.

They have attempted to develop a theory which is suitable for making predicitions using only parameters which can be estimated in advance. The basic parameters used in the theory are the constants in the Mark Houwink equation (equation 19) for the intrinsic viscosity of a polymer in a given solvent.

$$[\eta] = KM^{\alpha} \qquad \text{------} \; (19)$$

where K and α are constants.

$[\eta]$ is the intrinsic viscosity

M is the molecular weight.

The constants K and α are reasonably well tabulated although not all the common polymer-solvent combinations have been studied.

Although their model is written in mathematical terms some of their derivations were intuitive and they expect that the theory will need refining in the light of experimental results. At present the calculations are somewhat involved and the results quoted in the paper were from a computor. They hope that they can simplify the model so that once the concepts are understood, calculations can be made by hand. In their paper they derive the equations necessary for the prediction of the time required for an initial molecular scale dispersion of a polymer in a liquid diluent to become noticeably demixed.

They calculated the rate at which a given polymer-"solvent" dispersion coagulates and used the results to estimate the time for the mixture to develop a noticeable turbidity. The calculations required estimates of the viscosity of the mixture and the rate of diffusion of the polymer in the particular system and methods for computing them have been briefly described. Estimates of the viscosity and the diffusion coefficients required a knowledge of the polymer molecular weight, amorphous density, solvent viscosity and the Mark-Houwink coefficients for the particular polymer and solvent. Predicitions of the turbidity of the polymer-solvent mixtures required, in addition, values for the refractive indices of the liquid and polymeric components.

The results obtained by using the model were in qualitative agreement with practical experience and the limited laboratory data available for comparison. They expressed the hope that the foundations laid by their work would be built upon to develop better methods for predicting polymer solubility.

2:2 EXPERIMENTAL.

2:21 MATERIALS.

BENZENE.

Analar benzene (Fisons Ltd.) was used without further purification.

ϵ CAPROLACTAM.

ϵ caprolactam (Courtaulds Ltd.) was recrystallised twice from benzene, dried in a vacuum oven at room temperature, and stored in a vacuum descicator over phosphorus pentoxide.

LAUROLACTAM.

Laurolactam (Hülls Ltd.) was purified in the same way as caprolactam.

SODIUM HYDRIDE.

Sodium hydride (Koch-Light Ltd.) was used without further purification. It was stored and handled in a glove box through which a continuous stream of dry 'white spot' nitrogen was passed. The glove box contained beakers of phosphorus pentoxide and silica gel to maintain a dry atmosphere.

N - ACETYL CAPROLACTAM.

N- acetyl caprolactam (Courtaulds Ltd.) was dried by refluxing over calcium hydride for three hours under a 'white spot' nitrogen pressure of 3mm Hg, distilled at 190°/10mm Hg, and stored over calcium hydride. Hydrolysis with aqueous sodium hydroxide followed by back titration with perchloric acid indicated 100% purity. A gas liquid chromatograph run on a Pye Series 104 chromatograph gave a single peak.

$$N_D^{25} = 1.4882$$

CUMENE (ISOPROPYL BENZENE)

Cumene (Fisons S L R Grade) was used without further purification. Its vapour was used to provide a constant temperature, 150° C, in the polymensation apparatus.

p CYMENE.

p Cymene (Fisons Technical Grade) was used without further purification.

POLYMERS

Commercial polymers, listed in Table 1, were used after drying overnight in a vacuum oven at room temperature.

TABLE 1

POLYMER.	TRADE NAME/GRADE.	SUPPLIER.
POLYSTYRENE	LUSTREX HFSS	MONSANTO
POLYMETHYL METHACRYLATE	DIAKON MO900	I.C.I
NITRILE RUBBER	BREON 1042	B.P.PLASTICS
POLYCARBONATE	MAKROLON	BAYER
POLYBUTADIENE	BR 1200	SHELL
POLYISOPRENE	CARIFLEX	SHELL
POLYETHYLENE		
HIGH DENSITY	XDG -33	I.C.I
LOW DENSITY	RIGIDEX TYPE 25	B.P.PLASTICS
POLYPROPYLENE	PROPATHANE GWE 105	I.C.I.
POLYEPICHLOROHYDRIN	HYDRIN 100	B.F.GOODRICH.
EPICHLOROHYDRIN/ ETHYLENE OXIDE COPOLYMER.	HYDRIN 200	B.F. GOODRICH.
POLYVINYL CHLORIDE	WELVIC	I.C.I.
NATURAL RUBBER	SM SMOKED RUBBER RSS1	HUBRON RUBBER CHEMICALS.
NYLON 12	VESTAMID L1801	HÜLLS.
NYLON 6	MARANYL F/106	I.C.I.
NYLON 66	MOULDING GRADE	I.C.I
NYLON 6, 10	MARINYL B/100	I.C.I.
NYLON 11	RILSAN BMNO	I.C.I.
POLYSULPHONE	P1700 P3500	B.X.L.
POLYCHLOROPRENE	NEOPRENE W	Du PONT.
STYRENE-BUTADIENE (S.B.R.)	INTOL 1500	I.S.R.
STYRENE-BUTADIENE (HIGH STYRENE RESIN)	POLYSAR SS 250	POLYMER CORPORATION
IMPACT STYRENE	LUSTREX HT 42-1	MONSANTO

TABLE 1 CONTINUED.

POLYMER.	TRADE NAME/GRADE.	SUPPLIER.
3-3 BIS(CHLOROMETHYL) 1- OXACYCLOBUTANE	PENTON	HERCULES.
SILICONE RUBBER	SILICONE RUBBER E.300	I.C.I
S.B.S.THERMOPLASTIC RUBBER	PH104 - 1001 TR 3202 NATURAL TR 2104-1001 TR 5151 NATURAL	SHELL
STYRENE - ACRYLONITRILE	TYRIL 790	DYSTRENE LTD.
ETHYLENE VINYLACETATE COPOLYMERS	ETHYLENE-VINYLACETATE	
(1) 28% VINYL ACETATE.	28-05	I.C.I
(2) 40% VINYL ACETATE.	40-50	I.C.I.
POLYETHYLENE OXIDE	POLYOX.	CARBIDE.
POLYPHENYLENE OXIDE	PPO	GENERAL ELECTRIC
POLYETHYL ACRYLATE	CYANACRYL L	AMERICAN CYANAMID CO.

2:22 THE SOLUBILITY OF POLYMERS IN LACTAMS.

The solubility of polymers in caprolactam and laurolactam was studied in a vapour heated polymerisation tube fitted with a nitrogen bubbler and a nitrile rubber seal.

The required weights of lactam monomer and polymer (10% by weight) were weighted into a polymerisation tube and dried in a vacuum oven at room temperature overnight. The tube was then fitted with a nitrogen bubbler and placed in a constant temperature bath (the vapour of boiling cumene - 150°C). Figure 1. Nitrogen bubbling through the liquid gave sufficient agitation to help solution formation. If the polymer dissolved, the tube was removed from the constant temperature bath as soon as solution was complete. If, after four hours, the polymer showed no signs of dissolving, it was considered to be insoluble and the polymerisation tube was removed from the constant temperature bath. For polymers which had partially dissolved, more time was allowed to see if a solution could be obtained.

2:23 THE POLYMERISATION OF LACTAM MONOMERS IN THE PRESENCE OF DISSOLVED POLYMERS.

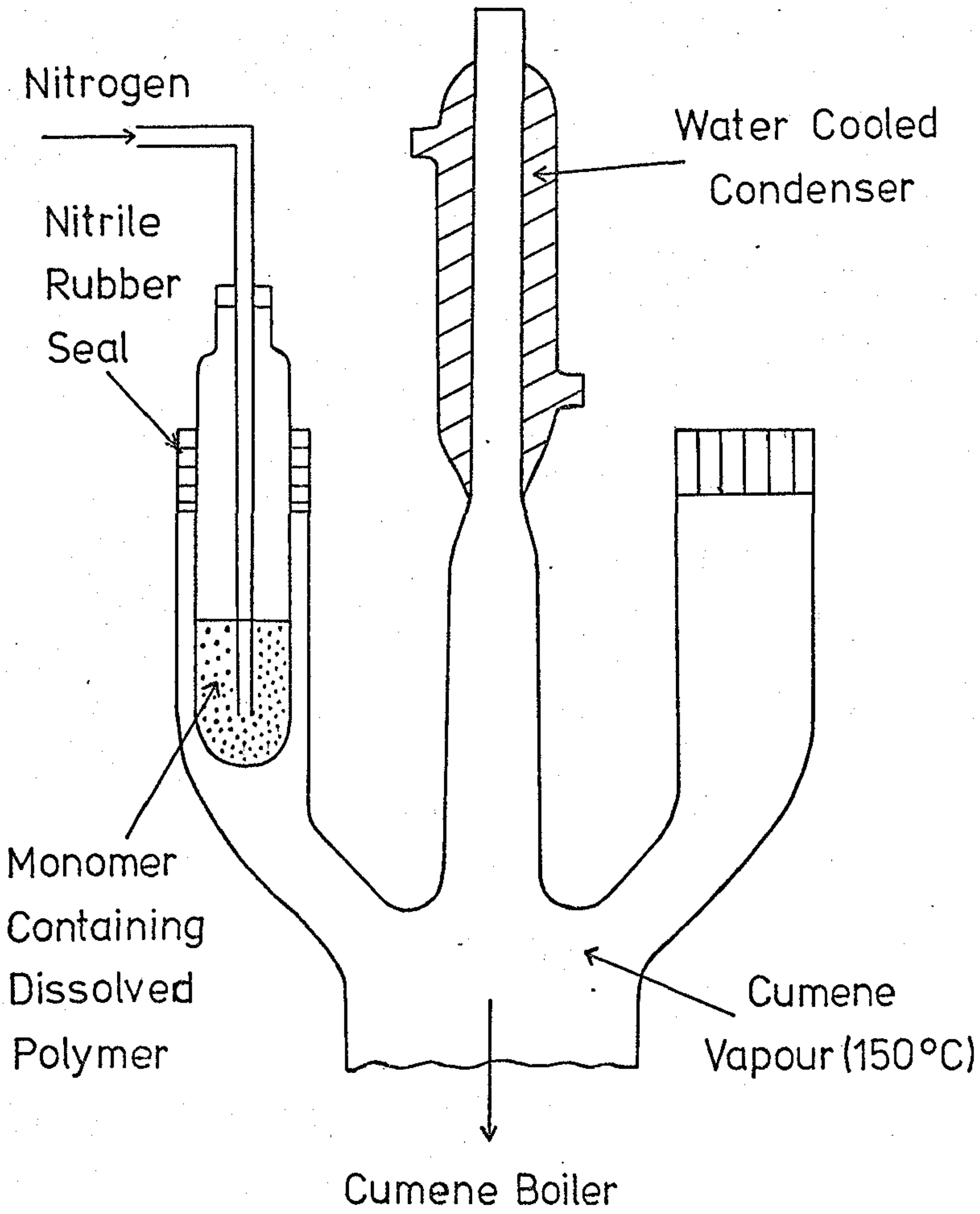
When a polymer dissolved in either caprolactam or laurolactam an attempt was made to polymerise the monomer in its presence. Sodium hydride was used as the catalyst and, where necessary, N-acetyl caprolactam was used as the cocatalyst. In all the attempted polymerisations the amount of the second component was 10% by weight.

The required weights of polymer and lactam monomer were weighed into a polymerisation tube and dried in a vacuum oven at room temperature overnight. The polymerisation tube was then fitted with a nitrogen bubbler and placed in a constant temperature bath (150 ± 0.5°C, the vapour of boiling cumene). When all the polymer had dissolved the sodium hydride was added. The catalyst was stored in a glove box large enough to contain a four figure balance so that it could be weighed into a weighing bottle in an inert atmosphere. The actual weight of sodium hydride added was weighed by difference, the weighing bottle being weighed before and after the addition on a four figure balance in a balance room. This method for weighing the sodium hydride catalyst was used for all the polymerisations described in this thesis. In all the attempted polymerisations the catalyst concentration was 2 mole %.

In the most simple case the catalyst reacted with the monomer to form lactam anions, hydrogen being evolved. When all the catalyst had reacted, indicated by the evolution of no more bubbles of hydrogen, the N- acetyl caprolactam was added from a microsyringe. The amount of cocatalyst used in all the attempted polymensations in which it was used was 0.3 mole %. Polymerisation was initiated almost as soon as the cocatalyst had been added and the viscosity of the solution started to increase after about four minutes. The polycaprolactam had crystallised after about twenty minutes and the experiment was stopped after one hour.

FIGURE 1

SCHEMATIC POLYMERISATION APPARATUS



DIMENSIONS OF POLYMERISATION TUBE

Length 210 mm

Internal Diameter 18 mm

When polysulphone was the dissolved polymer and caprolactam the monomer it was found that polymerisation occured without the addition of a cocatalyst.

If the catalyst reacted with the dissolved polymer more readily than with the monomer, usually indicated by the production of an intense colour, the experiment was stopped. For these polymers the lactam anions have to be formed in a separate vessel for polymerisation to occur. The required weight of polymer, together with part of the monomer, were weighted into a polymerisation tube. The remainder of the monomer was weighed into a separate polymerisation tube. After drying overnight in a vacuum oven at room temperature the tubes were fitted with nitrogen bubblers and placed in a constant temperature bath. (150 ± 0.5°C). When all the polymer had dissolved in the monomer the required weight of sodium hydride catalyst was added to the monomer in the second polymerisation tube. When all the catalyst had reacted the solution containing the lactam anions was added to the polymerisation tube containing the polymer solution and thoroughly mixed. The required volume of N-acetyl caprolactam was then added from a microsyringe and the viscosity of the solution started to increase after about four minutes. After twenty minutes the polycaprolactam had crystallised and the experiment was stopped after an hour.

With caprolactam as the monomer and polycarbonate as the dissolved polymer, polymerisation occured without the addition of a cocatalyst.

2:24 CAPROLACTAM POLYMERISATION AT 176°C.

The required weight of caprolactam was weighed into a polymerisation tube and dried overnight in a vacuum oven at room temperature. The tube was then fitted with a nitrogen bubbler and placed in a constant temperature bath (176° C, the vapour of boiling p cymene). When all the caprolactam had melted the required weight of sodium hydride was added in the usual way.and the solution was held at 176°C for two hours. If the viscosity of the solution started to increase, indicating that polymerisation was taking place the nitrogen bubbler was raised above the level of the liquid. A nitrogen atmosphere was maintained above the polymerising monomer for the duration of the experiment to prevent oxidation. Two hours after adding the catalyst the polymerisation tube was removed from the constant temperature bath and cooled quickly by plunging it into liquid nitrogen.

2:25 MONOMER CONVERSION.

The contents of the polymerisation tube were placed in a beaker and dried in a vacuum oven at room temperature overnight. They were then weighed by difference into a soxhlet extraction thimble and the unreacted monomer was removed by extracting for 24 hours with water in a soxhlet extraction apparatus. The contents of the extraction thimble were then washed into a weighed beaker with distilled water, evaporated to dryness in an oven and dried to constant weight in a vacuum oven.

2:3 RESULTS AND DISCUSSION.

2;31 POLYMER SOLUBILITY IN LACTAM MONOMERS.

The results of the solubility experiments are shown in Tables 2 - 5.

TABLE 2.

POLYMERS SOLUBLE IN CAPROLACTAM AT 150°C.

POLYSTYRENE
POLYMETHYL METHACRYLATE
POLYCARBONATE
STYRENE-ACRYLONITRILE COPOLYMER.
PENTON
IMPACT STYRENE[a]
NYLON 11
POLYSULPHONE
THERMOPLASTIC RUBBERS.
NYLON 12

a). mobile solution, well dispersed (cross-linked butadiene in a materials did not dissolve.

TABLE 3.

POLYMERS INSOLUBLE IN CAPROLACTAM AT 150°C.

NITRILE RUBBER[a]
POLYBUTADIENE
POLYISOPRENE
HIGH DENSITY POLYETHYLENE
LOW DENSITY POLYETHYLENE
POLYPROPYLENE
POLYVINYL CHLORIDE[b]
SILICONE RUBBER
HYDRIN 100
HYDRIN 200
NATURAL RUBBER
POLYPHENYLENE OXIDE
NYLON 6,6
NYLON 6,10
STYRENE BUTADIENE[c] (HIGH STYRENE RESIN)
POLYCHLOROPRENE[c]
STYRENE BUTADIENE[c] (SBR)
ETHYLENE VINYLACETATE COPOLYMERS
POLYETHYLENE OXIDE
POLYETHYL ACRYLATE
POLYCHLOROPRENE

a). slightly soluble, but not soluble to an extent of 10% by weight

b). decomposes at 150°C.

c). swollen gel.

TABLE 4

POLYMERS SOLUBLE IN LAUROLACTAM AT 150°C.

POLYSTYRENE

POLYMETHYL METHACRYLATE

STYRENE-ACRYLONITRILE COPOLYMER

NYLON 6

NYLON 11

PENTON

THERMOPLASTIC RUBBERS

ETHYLENE-VINYLACETATE COPOLYMERS

IMPACT STYRENE[a]

a) mobile solution well dispersed (cross linked butadiene did not dissolve)

TABLE 5.

POLYMERS INSOLUBLE IN LAUROLACTAM AT 150°C.

NITRILE RUBBER[a]

POLYCARBONATE

POLYBUTADIENE

POLYISOPRENE

HIGH DENSITY POLYETHYLENE

LOW DENSITY POLYETHYLENE

NATURAL RUBBER

POLYVINYL CHLORIDE[b]

HYDRIN 100

HYDRIN 200

POLYPROPYLENE

POLYSULPHONE

POLYETHYL ACRYLATE

NYLON 6,6

STYRENE-BUTADIENE[c] (SBR)

NYLON 6,10

POLYETHYLENE OXIDE

POLYPHENYLENE OXIDE

SILICONE RUBBER

POLYCHLOROPRENE[c]

STYRENE BUTADIENE[c] (HIGH STYRENE RESIN)

a) slightly soluble, but not soluble to an extent of 10% weight

b) decomposes at 150°C

c) swollen gel

Before the results of the solubility experiments are discussed some observations on the use of solubility parameters in predicting polymer solubility will be given. Although the literature indicates that solubility parameters are useful in predicting polymer solubility it will be shown that the method has limitations.

The results to compile Table 6 were taken from the Polymer Hand book[87] and lists values of the solubility parameters for some of the polymers considered in this work. They indicate that there is a large range for the calculated and determined values of the solubility parameters, even for well studied polymers like polystyrene and polymethylmethacrylate. All the data in Table 6 were calculated, or measured at 25°C.

One of the first attempts to calculate polymer solubility parameters was that of Small.[88] This method is limited as it can only be used for polymers in which there are no dipole interactions and /or hydrogen bonding. Small indicated that the biggest source of error in his calculations was polymer density because there was little reliable density data, even for well characterised polymers. With the increase in data which has occurred it should be possible to quote accurate values for the solubility parameters for some polymers. Instead, Small's original values are still quoted.

As Small's method has only limited usefulness much work has been done in the last ten years to produce a satisfactory equation for calculating solubility parameters in which hydrogen bonding and dipole interactions occur. Although several equations have been proposed a satisfactory solution has not yet been discovered.

TABLE 6.

POLYMER SOLUBILITY PARAMETERS AT 25°C.

	EXPERIMENTAL.			CALCULATED.		
POLYMER	HIGH	Single Value only.	LOW	HIGH	Single value only.	LOW.
POLYSTYRENE.	9.7		8.5	10.3		9.12
POLYMETHYL-METHACRYLATE.	12.84		9.0		9.25	
NITRILE RUBBER.						
80 : 20		9.5			9.0	
75 : 25	9.50		9.38		9.25	
70 : 30	9.90		9.38			
POLYBUTADIENE.	8.6		8.1	8.38		7.16
CIS 1-4 POLYISOPRENE.	10.0		7.9	8.15		7.42
NYLON 6,6		13.6				
POLYVINYL CHLORIDE	10.8		9.38	9.55		9.42
STYRENE-BUTADIENE						
85 : 15	8.55		8.40	8.51		8.48
75 : 25	8.60		8.10	8.58		8.54.
60 : 40	8.70		8.55	8.68		8.65
POLYETHYLENE	8.35		7.70	8.2		8.0
POLYPROPYLENE	9.2		8.1		9.4	
POLYCHLOROPRENE	9.25		8.2	9.38		8.11
NATURAL RUBBER	8.35		7.9			
POLYACRYLONITRILE	15.4		12.5		12.75	

Although there are several methods for the experimental determination of solubility parameters none of them are standard methods. The methods do not take into account differences due to molecular weight, temperature and pressure. Because of this most of the values quoted in books are average values, no mention being made of the method of determination or the molecular weight of the polymer. If they are to be of any value polymer solubility parameters should be measured using a well defined test method which fully describes the polymers being studied.

In theory a polymer should dissolve in a solvent if their solubility parameters are similar. Caprolactam and laurolactam melt at 69° and 150°C respectively, and in this work the solubility experiments were performed at 150°C. If the published solubility parameters are to be used to predict polymer solubility,experiments should be performed at 25°C. The usefulness of the solubility parameter data is therefore restricted to a small temperature range as little indication is given in the literature of how the values vary with temperature. If solubility experiments are to be performed at 150° the data used to predict polymer solubility should also be at this temperature.

There are several reasons why the solubility experiments were performed at 150°C. If the results for caprolactam and laurolactam are to be compared then they should be performed at the same temperature. The melting points of caprolactam and laurolactam are 69° and 150°C respectively so that the lowest temperature at which the experiements can be performed is 150°C.

It will be shown (page 79) that at 176°C caprolactam can be polymerised by an anionic mechanism without the use of a cocatalyst, the degree of polymerisation depending on the catalyst concentration and polymerisation time. Also, if caprolactam is polymerised below 150°C the polymer precipitates in the monomer.[64,103] As laurolactam can be polymerised successfully at 150°C by an anionic mechanism[104] this was chosen as the temperature at which the solubility experiments were performed.

The results of the solubility experiments can be discussed in terms of polymer solubility parameters, hydrogen bonding and polymer crystallisation. Although the values of the solubility parameters which are given in the literature cannot be used directly to explain the results of the solubility experiments they can be used to show trends. The results give an indication of the range of values of the solubility parameters for which the polymers are soluble in the monomers. As the results of the solubility experiments are similar they will be discussed for caprolactam and then, where differences occur, they will be discussed separately.

The value of the solubility parameters for monomers and solvents will be expected to decrease markedly with an increase in temperature. The factors affecting the solubility parameter, the vapour pressure and the density, change quite appreciably with temperature. The value of the solubility parameter for caprolactam at 25°C is 12.7[87] and it might be expected that this will drop below 10 at 150°C. Although there will be changes in the solubility parameters for polymers they will not be as large as for the monomers and solvents.

The solubility experiments show that most hydrocarbon polymers are insoluble in caprolactam. The value of the solubility parameters for polymers such as polyethylene and polybutadiene are usually at the lower end of the scale. Even though the value of the solubility parameter for caprolactam will be decreased at 150°C more than for the polymers mentioned, the values will never be close enough that the polymers will be soluble. Also, there is no possibility of hydrogen bonding for polymers of the type mentioned above. Hydrogen bonding aids solubility and can be a deciding factor if a polymer is on the limits of solubility. Caprolactam made no impression on the thermoplastics but the rubbers were slightly swollen.

The values of the solubility parameter given in Table 6 indicate how unrealistic some of the quoted values are. If polyisoprene really did have a solubility parameter of 10 it would be expected to be at least partially soluble in caprolactam at 150°C. The value of 8.2, which is the value usually quoted at 25°C is much more realistic and in line with the observed experimental results.

Polychloroprene, with a solubility parameter of 9.2 at 25°C, would be expected to be partially soluble in caprolactam. The polymer, although considerably swollen and partially soluble, never gave signs of being soluble to an extent of 10% by weight. The hydrogen bonding capacity of chlorinated hydrocarbons is poor[105] so it will be expected that chlorinated hydrocarbons will have a small but negligible, hydrogen bonding index.[106]

Because of this there will be little contribution from hydrogen bonding to aid solubility. A factor which could also affect the solubility is that polychloroprene cross-links on standing. Although this can be removed on milling the results showed that it was still not possible to obtain a 10% solution.

The introduction of certain components in the form of copolymers aids solubility even though the polymers are still rubbers. As an example, the value of the solubility parameters for styrene-butadiene rubbers are only slightly greater than those for the hydrocarbon polymers yet they are considerably swollen by the monomer. The polystyrene component of the rubber is dissolved by the caprolactam causing swelling and partial solubility.

Nitrile rubbers, because of the much higher value of the solubility parameter for acrylonitrile than polystyrene, are more soluble in caprolactam than styrene-butadiene rubbers. As the solubility parameter is increased there is solubility rather than swelling. The solubility experiments indicated that if the butadiene content is high, solubility to the extent of 10% by weight will never be achieved. It is known that when nitrile rubbers are prepared[107] a "two phase system" results and copolymers with high and low acrylonitrile contents are formed. The partial solubility might therefore be due, in part, to the greater insolubility of the copolymer fraction with the high butadiene content.

As indicated in the introduction to this section, solubility is expected to occur when the solubility parameters of the polymer and solvent are similar.

Polystyrene, polymethyl-methacrylate and styrene-acrylonitrile are all readily soluble in caprolactam. The values of the solubility parameters for polymethyl methacrylate and polystyrene are about 9.3 and 9.5 respectively at 25°C. The value for styrene-acrylonitrile copolymers varies with their composition but is expected to be about 9.7 at 25°C. For polymethyl methacrylate hydrogen bonding will be expected to aid solubility but this will not be the case for polystyrene and styrene-acrylonitrile because of the small value of their hydrogen bonding index. The values of the solubility parameters will be slightly reduced at 150°C so that it would be expected from the observed solubilities that the value of the solubility parameter for caprolactam would be about 9.2.

Polycarbonate and polysulphone are both soluble in caprolactam at 150°C. Solvents which readily dissolve these polymers have solubility parameters of about 9.2 at 25°C. If the values of the solubility parameters for polysulphone and polycarbonate are between 9.3 and 9.7 at 25°C both would be expected to be soluble in caprolactam and this is what is observed.

The results of the solubility experiments discussed so far can be used to indicate a lower limit to the value of the solubility parameter for which polymers are soluble in caprolactam. Taking into account the decrease in the value of the solubility parameter with temperature it would appear that a value of about 8.8.at 150°C is a suitable lower limit.

Some of the copolymers considered contained a considerable amount of a rubbery component, such as polybutadiene and it is difficult to predict what would happen if the polymers contained only a small amount of rubber. It is suggested that there will be a butadiene content such that solubility will be critical in caprolactam at 150°C.

As styrene-acrylonitrile is soluble in caprolactam at 150°C it would suggest that the upper limit of the value of the solubility parameter is above 9.7, and a value of about 10 is indicated.

The solubility of the nylon polymers in caprolactam is interesting. The ability of nylons 11 and 12 to dissolve is due to the nearness of their melting points to the temperature at which the solubility experiments were performed. The melting points of nylon 11 and nylon 12 are 174° and 178°C respectively. The temperature at which the solubility experiments were performed is high enough to reduce the crystallinity and make them soluble. The solubility is of course aided by hydrogen bonding. For nylon 6,6 and 6,10, with crystalline melting points of 267° and 226°C respectively, the difference in temperature is such that the reduction in crystallinity is small and the polymers are insoluble. Even though there is hydrogen bonding in the solution its effect is not strong enough to cause solubility.

Polyphenylene oxide, with a solubility parameter similar to that of polystyrene, is a polymer which would be expected to be soluble if only solubility parameters are important.

From the observations made during the solubility experiments it appeared that the polymer dissolved and then crystallised out. It might be that the polyphenylene oxide used in the solubility experiments, the original polyphenylene oxide prepared from 2,6 Xylenol, is unsuitable because of its high softening point. The newer polymers with lower softening points might be more suitable and give interesting systems.

Although polyvinyl chloride decomposes at 150°C it is unlikely that the polymer would be soluble because its crystallinity must be destroyed before solubility can occur. Also, as the hydrogen bonding index for polyvinyl chloride is small there will be little hydrogen bonding to aid solubility.

When laurolactam was used as the solvent the results were similar to those for caprolactam, with the following exceptions.

Polycarbonate and polysulphone are insoluble in laurolactam whereas they are soluble in caprolactam. It would be expected that, because of its structure, the value of the solubility parameter for laurolactam will be lower than that for caprolactam. The range of polymer solubility parameters for which polymers would be expected to be soluble is therefore lower for laurolactam. Polycarbonate and polysulphone, with solubility parameters of about 9.5, will be close to the upper limit for laurolactam and it was found that the polymers were only partially soluble in the monomer. The lower range of solubility parameters would also explain why the ethylene-ethyl acrylate copolymers are soluble in laurolactam but not caprolactam. The values of the solubility parameters for polyethylene and ethyl acrylate monomer at 25°C are 8.0 and 8.9 respectively so that the value of the solubility parameter of the copolymers is expected to be about 8.5 at 150°C.

From the crystalline melting points of the nylon homopolymers it would be expected that nylon 6 would be insoluble in laurolactam at 150°C whereas it dissolved readily. Nylon 6 has a crystalline melting point similar to that of nylon 6,10 which is insoluble in laurolactam so that other factors must be involved for nylon 6 to be soluble. It would be expected that the reduction in crystallinity and hydrogen bonding of nylon 6 would not be enough to cause solubility. The reason for the solubility of nylon 6 in laurolactam must therefore be specifically associated with the similarity of the monomers. Nylon 6 is soluble in its own monomer at 150°C.[64,103] It is not surprising therefore, that nylon 6 is soluble in laurolactam at the concentrations employed.

Although the range of solubility parameters for which polymers are soluble in laurolactam is lower than that for caprolactam it is not expected that copolymers such as nitrile rubber and styrene-butadiene rubber would be soluble because of their insoluble rubber components.

The results suggest a range of solubility parameters for which polymers are soluble in caprolactam and laurolactam. They show that diene rubbers, or copolymers in which one of the components is a diene rubber are usually insoluble in the monomers. The solubility of crystalline, or partially crystalline polymers is usually dependent on a reduction in crystallinity and hydrogen bonding. Amorphous polymers, especially those containing polystyrene, appear to be particularly soluble in both monomers. The value of the solubility parameters for styrene-acrylonitrile copolymers would suggest that they might not be soluble in laurolactam at 150°C, whereas they are readily soluble to 10% by weight.

The unexpected solubility suggests some special influence of the styrene or acrylonitrile units.

Although the values of the solubility parameters of polymers change with temperature the results indicate that for high molecular weight polymers the change can be small. It could be held that the factor which has the most influence on the value of a polymer solubility parameter is molecular weight. This would explain the large range of values of solubility parameters for a given polymer which are quoted in the literature. The results also show that in certain cases hydrogen bonding and polymer crystillinity can have a marked effect on polymer solubility.

Therefore, although polymer solubility parameters are useful, more accurate experimental data and understanding of solubility are needed to explain the observations described above. In the absence of a fuller understanding of solubility the following table lists the "best" values of solubility.parameters of several polymers at 150°C.

TABLE 7.

ESTIMATED POLYMER SOLUBILITY PARAMETERS AT 150°C.

POLYMER	POLYMER SOLUBILITY PARAMETER	POLYMER	POLYMER SOLUBILITY PARAMETER
POLYSTYRENE	9.3	STYRENE ACRYLONITRILE COPOLYMER	9.7
POLYMETHYL METHACRYLATE	9.1	ETHYLENE-ETHYLACRYLATE COPOLYMERS	8.5
POLYSULPHONE	9.4		
POLYCARBONATE	9.6	POLYCHLOROPRENE	8.8
POLYISOPRENE	8.1	POLYBUTADIENE	8.2

2:32 THE POLYMERISATION OF LACTAM MONOMERS IN THE PRESENCE OF DISSOLVED POLYMERS.

It was found that four methods were needed in order to polymerise the lactam monomers in the presence of all the polymers that were soluble in them. The methods are summarised below and the results are given in Tables 8 and 9.

METHODS OF POLYMERISATION.

A. Sodium hydride is added to a solution of the polymer in the monomer, bubbles of hydrogen are evolved but no polymerisation occurs. When N-acetyl caprolactam is added to the solution rapid polymerisation occurs.

B. Sodium hydride is added to a solution of the polymer in the monomer, bubbles of hydrogen are evolved and polymerisation occurs without the addition of a cocatalyst.

C. When the catalyst reacts with the dissolved polymer the lactam anions are formed in a separate vessel and then added to the polymer solution. Rapid polymerisation occurs when the N-acetyl caprolactam cocatalyst is added.

D. Lactam anions, formed in a separate vessel, are added to the polymer solution and polymerisation occurs without the addition of a cocatalyst.

TABLE 8.

CAPROLACTAM POLYMERISATION IN THE PRESENCE OF DISSOLVED POLYMERS.

POLYMER:	METHOD OF POLYMERISATION.	POLYMER.	METHOD OF POLYMERISATION.
POLYSTYRENE	A	NYLON 11	A
POLYMETHYL METHACRYLATE	B C	NYLON 12	A
POLYCARBONATE	D	POLYSULPHONE	B
PENTON	A	IMPACT STYRENE	A
THERMOPLASTIC RUBBERS	A	STYRENE-ACRYLONITRILE COPOLYMER	B C

TABLE 9.

LAUROLACTAM POLYMERISATION IN THE PRESENCE OF DISSOLVED POLYMERS.

POLYMER.	METHOD OF POLYMERISATION.	POLYMER	METHOD OF POLYMERISATION.
POLYSTYRENE	A	NYLON 6	A
IMPACT STYRENE	A	NYLON 11	A
PENTON	A	THERMOPLASTIC RUBBERS	A
POLYMETHYL METHACRYLATE	B C	STYRENE-ACRYLONITE COPOLYMER	B C
ETHYLENE-VINYL ACETATE COPOLYMERS	B C		

When sodium hydride is added to caprolactam at 150°C sodium caprolactam is formed and bubbles of hydrogen are seen to be evolved. If the solution is maintained at 150°C polymerisation does not appear to take place, even when high catalyst concentrations are used and the solution is held for several hours. The fact that the contents of the polymerisation tube are still soluble in water confirms that no polymerisation has occurred.
When N-acetyl caprolactam is added to caprolactam which contains lactam anions at 150°C rapid polymersiation occurs. This is the anionic polymerisation of caprolactam using a catalyst and a cocatalyst, the mechanism of which is described in Appendix 1.

If caprolactam is polymerised in the presence of a dissolved polymer using a catalyst and cocatalyst as described in Method A the result is a polymer blend. The results in Table 8 indicate that it is possible to prepare blends with many of the polymers by this method. Method A is used when there is no reaction between the catalyst and the dissolved polymer.

If the method of polymerisation used is Method B it indicates that caprolactam can be polymerised in the presence of a dissolved polymer without the addition of a cocatalyst. When sodium hydride is added to a solution of caprolactam containing dissolved polysulphone rapid polymerisation is observed to take place, the rate of reaction being dependent on the catalyst concentration. As it had already been shown that caprolactam would not homopolymerise at 150°C without the addition of a cocatalyst it seemed likely that the polysulphone was acting as the cocatalyst.

As the original experiment was performed with polysulphone which had not been purified in any way it was possible that an additive was acting as a cocatalyst. An experiment was devised to show that it was the dissolved polymer which was acting as the cocatalyst in the reaction. A sample of reprecipitated polysulphone was dissolved in caprolactam and the solution was maintained at 150°C. To it was added caprolactam containing lactam anions which had been formed in a separate vessel, care being taken to ensure that all the sodium hydride had reacted. The solution containing the polysulphone polymerised in a time which was comparable with the original experiment (crystallisation occuring within 15 to 20 minutes depending on the catalyst concentration). Polymerisation can only occur if the polysulphone is acting as the cocatalyst for the reaction.

If the catalyst reacts more readily with the dissolved polymer than with the monomer the lactam anions must be formed in a separate vessel for polymerisation to occur. In Method C a cocatalyst must be used to polymerise the caprolactam and a polymer blend is formed.

If D is the Method of polymerisation the dissolved polymer acts as a cocatalyst in the polymerisation of caprolactam and the lactam anions must be formed in a separate vessel. Caprolactam can be polymerised in the presence of polycarbonate by this method. The use of polycarbonates as cocatalysts in caprolactam polymerisation has been described in the patent literature[69] but no indication of the composition of the polymers or the reaction mechanism is given.

Laurolactam can be polymerised in the presence of all the polymers soluble in it by Methods A and C, none of the polymers acting as cocatalyst for the reaction.

The results show that there are two factors determining the method of polymerisation of the lactam monomers. The first is the reactivity of the catalyst towards the dissolved polymer and the second is the ability of some polymers to act as cocatalysts in the polymerisation of caprolactam. If the catalyst reacts more rapidly with the dissolved polymer than with the monomer, the lactam anions must be formed in a separate vessel for polymerisation to occur. However, the major significance of the polymerisation experiments is the ability of the dissolved polymer to act as cocatalyst in the polymerisation of caprolactam. As the dissolved polymers act as cocatalysts it seems probable that copolymers will be formed.

After considering the results of the polymerisation experiments it was decided to follow two separate courses of work.

The first, and most important, was the polymerisation of caprolactam in the presence of dissolved polysulphone as the results of some solubility experiments indicated that polycaprolactam-polysulphone copolymers had been formed. Polymers were prepared in order

(a) to determine the copolymer composition
(b) to attempt to determine the reaction mechanism
(c) to make a microscopic study of the structure of the copolymers
(d) to study some of the physical properties of the copolymers and to compare them with a commercial nylon 6.

Secondly, polymer blends of polycaprolactam with polystyrene, impact styrene and SBS thermoplastic rubber were prepared. The blends were prepared in order

(a) to determine the polymer blend composition

(b) to make a microscopic study of the structure of the blends.

(c) to study some of the physical properties of the blends and compare them with polycaprolactam.

It was hoped that the preparation of blends with polystyrene present in different forms might provide information by which it would be possible to determine some of the factors governing polymer compatibility.with crystalline polymers.

2:33 CAPROLACTAM POLYMERISATION AT 176°C.

The aim of this experiment was to show that 150°C was the most suitable temperature at which to perform the solubility experiments and that increasing the temperature would produce a more complicated system. Attempts were made to polymerise caprolactam at 176°C using various catalyst concentrations but without the use of a cocatalyst. The contents of the polymerisation tubes were extracted with water in a soxhlet extraction apparatus and the amount of monomer converted to polymer for the various catalyst concentrations was calculated. The results given in Table 10, and illustrated in Figure 2, show that appreciable polymerisation can occur.

TABLE 10.

CAPROLACTAM POLYMERISATION AT 176°C WITHOUT THE USE OF A COCATALYST.

No.	CATALYST CONCENTRATION (MOLE %)	MONOMER CONVERSION (%)
A1	2.15	39.2
A2	1.38	39.9
A3	1.15	51.5
A4	0.58	37.4
A5	0.40	3.4
A6	1.15	46.4
A7	0.88	14.8
A8	2.53	86.7
A9	1.73	86.1

The lowest temperature at which the solubility of polymers in lactam monomers can be studied is 150°C because this is the melting point of laurolactam. Increasing the temperature at which the experiments are performed is expected to increase polymer solubility. However, when the monomers are polymerised in the presence of dissolved polymers reactions might occur which will complicate the interpretation of the results. Caprolactam cannot be polymerised at 150°C by an anionic mechanism without the use of a cocatalyst. The results of these experiments show that at 176°C caprolactam can be polymerised without the use of a cocatalyst, the amount of monomer converted to polymer depending on the catalyst concentration.

CAPROLACTAM POLYMERISATION AT 176°C

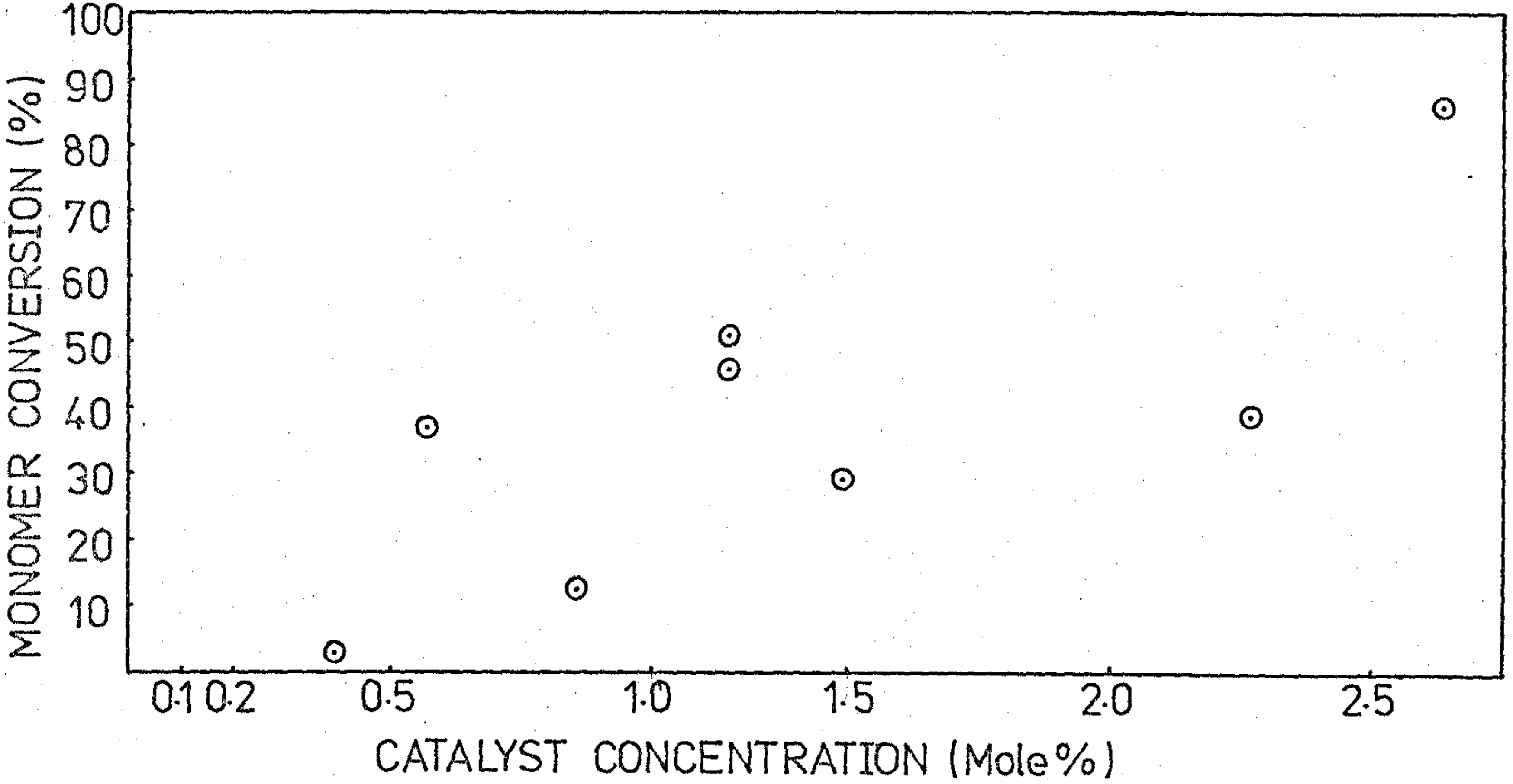


FIGURE 2

Although the results are scattered there is a steady increase in monomer conversion as the catalyst concentration is increased. The results of the experiments at 150°C show that some dissolved polymers can act as cocatalysts in the polymerisation of caprolactam with the formation of copolymers. If copolymers were prepared at 176°C they would be expected to contain some polycaprolactam due to homopolymerisation whereas, at 150°C all the polymer chains are initiated by the dissolved polymer. Any polycaprolactam homopolymer present in the copolymers prepared at 150°C will be formed by the degradation reactions described in the mechanism of the anionic polymensation of caprolactam (Appendix 1) but this is expected to be negligible under the reaction conditions used. 150°C is therefore the most suitable temperature at which to perform the solubility and polymerisation experiments.

3. POLYSULPHONE - POLYCAPROLACTAM COPOLYMERS.

3:1 EXPERIMENTAL.

3:11 MATERIALS.

∈ CAPROLACTAM. SODIUM HYDRIDE. CUMENE. BENZENE.	were purified as described previously (page 52)

METHANOL.

Filtered technical grade methanol (Fison's Ltd.) was used for polymer precipitation.

1.2 DICHLOROETHANE.

1.2 dichloroethane (Hopkins and Williams G.P.R.) for molecular weight determinations, was distilled once, the fraction boiling between 82.5 and 83.5°C being collected.

CHLOROFORM.

Chloroform (Fison's SLR Grade) for use in the soxhlet extraction of uncombined polysulphone, was used without further purification.

m CRESOL.

m Cresol (Fison's SLR Grade) was purified by distilling once under vacuum at 70°C/3mm Hg and stored in dark bottles out of sunlight.

CHLOROFORM.

Chloroform (Fison's "Analar" Grade) for use in determining the solution properties of polymers containing polysulphone, was used without further purification.

FORMIC ACID.

Formic Acid (Fison's 'Analar' Grade 98%) was used without further purification.

TOLUENE.

Toluene (Fison's 'Analar' Grade) was used without further purification.

4,4' DICHLORODIPHENYL SULPHONE.

4.4' dichlorodiphenyl sulphone (I.C.I.Ltd) was reprecipitated once from benzene, dried in a vacuum over at room temperature, and stored in a vacuum descicator.

DIPHENYL SULPHONE.

Diphenyl sulphone (Kodak Ltd.) was used without further purification. It was dried overnight in a vacuum oven at room temperature before use.

4.4' DIAMINODIPHENYL SULPHONE.

4.4' diaminodiphenyl sulphone (I.C.I.Ltd.) was used without further purification.

DIPHENYL ETHER.

Diphenyl ether (B.D.H.Ltd.) was used without further purification.

POLYSULPHONE.

Two grades of polysulphone, P1700 and P3500, were kindly supplied by B.X.L. They were dried overnight at room temperature in a vacuum oven before use.

3.12 THE PREPARATION OF POLYCAPROLACTAM-POLYSULPHONE COPOLYMERS.

Copolymers were prepared by polymerising caprolactam at 150°C in the presence of polysulphone, using sodium hydride as the catalyst and the dissolved polymer as the cocatalyst. Two types of polycaprolactam-polysulphone copolymers were made. The first type were prepared containing 10% by weight of polysulphone, with various catalyst concentrations, and polymerisation times of 1,2 and 4 hours. The second type, containing 5,10 and 15% by weight of polysulphone respectively, were prepared with fixed catalyst concentrations and polymerisation times.

The required amounts of polysulphone and caprolactam were weighed as solids into a glass polymerisation tube and dried overnight in a vacuum oven at room temperature. The polymerisation tube was then fitted with a nitrogen bubbler and placed in a constant temperature bath (150°C ± 0.5°C, the vapour of boiling cumene). While the polysulphone was dissolving some of the caprolactam vapourised and then condensed on colder parts of the polymerisation tube. Not all of this could be returned to the melt so the amount of caprolactam weighed into the polymerisation tube was such that, when the final polymer was weighed, the polysulphone content would be within certain specifications. When all the polysulphone had dissolved the sodium hydride catalyst was added by the method described previously (page 57).

As the polysulphone acted as the cocatalyst it was essential to ensure that the catalyst was thoroughly mixed in as soon as possible after it was added. Polymerisation could, in theory, start as soon as the sodium salt of caprolactam had been formed. When all the sodium hydride had reacted, indicated by the evolution of no more bubbles of hydrogen, the solution viscosity appeared to be unchanged. When the viscosity of the polymerisation mixture started to increase the nitrogen bubbler was raised so as to maintain an inert atmosphere in the upper part of the tube for the duration of the experiment. The polymerisation tube was removed from the constant temperature bath after the prescribed length of time and cooled within one minute. The polymer 'plug' was weighed as soon as possible after the polymerisation tube had been removed from the constant temperature bath.

3:13 CONVERSION OF MONOMER.

The amount of caprolactam converted to polycaprolactam was found by extracting shavings of the polymer with water in a soxhlet extraction apparatus. The shavings were obtained by turning the polymer on a lathe and had a thickness of about 0.2mm. About 2g of the polymer shavings were placed in a beaker and dried in a vacuum oven at room temperature overnight. The shavings had to be dried before the unreacted monomer was extracted because they absorbed water on standing in the atmosphere. The polymer was then weighed, by difference, into a soxhlet extraction thimble and the unconverted material was removed by extracting the shavings for 24 hours using water as the solvent. The contents of the extraction thimble were then transferred to a weighed beaker, evaporated to dryness in an oven, and then dried in a vacuum oven at 60°C overnight. The polymer was first weighed when the temperature of the oven had dropped to room temperature. The polymer was then dried for further periods of 6 hours at room temperature to constant weight.

3:14 DETERMINATION OF THE AMOUNT OF POLYSULPHONE COMBINED WITH POLYCAPROLACTAM.

For the polymers prepared containing 5, 10 and 15% by weight of polysulphone it was found necessary to use two techniques to extract the uncombined polysulphone.

For the polymers prepared containing 10 and 15% polysulphone the uncombined polysulphone could be removed by simple chloroform extraction. Dried polymer shavings (about 4g) from the monomer conversion experiments were weighed by difference into a soxhlet extraction thimble and then extracted for 3 days using chloroform as the solvent. The polymer shavings were then dried and weighed in the same way as in the monomer conversion experiments.

When the polysulphone concentration was 5% by weight it was impossible to extract the uncombined polysulphone by simple chloroform extraction. A detailed discussion on the reasons for this is given in the section on optical microscopy, Polymer shavings from the monomer extraction experiments were weighed and then dissolved in a mixture of formic acid and chloroform. After reprecipitation in methanol the polymer was filtered into a soxhlet extraction thimble and extracted for 3 days with chloroform. The polymer was then dried and weighed in the way described for the other extraction experiments.

3:15 HYDROLYSIS OF THE COPOLYMERS.

The copolymers to be hydrolysed had first been extracted with water to remove any unreacted caprolactam and then with chloroform to remove any uncombined polysulphone. About 4g. of the copolymers were refluxed with hydrochloric acid (80ml. 50/50 by volume of concentrated acid) for 40 hours. After 40 hours the reaction mixture was cooled and the contents of the flask washed into a litre beaker with a large volume of distilled water. The contents of the beaker were filtered through a No.4 sintered glass crucible, washed with more distilled water and then dried in a vacuum oven. The solution was evapourated to dryness and the compound obtained dried in a vacuum oven at room temperature to remove the last traces of water.

A sample of polysulphone homopolymer was also refluxed with hydrochloric acid for 40 hours. The water insoluble component was filtered and dried as described above; the solution on evaporation to dryness showed there to be no water soluble compounds.

3:16 MOLECULAR WEIGHT DETERMINATIONS.

The molecular weights of the polysulphone components of the copolymers were determined at 37°C using a Hewlett-Packard (Type 302 B) vapour pressure osmometer. The solvent used was 1,2 dichloroethane and benzil was used as the calibration standard.

Before any determinations were made samples were dissolved in chloroform, filtered, precipitated in methanol, filtered again and then dried in a vacuum oven at room temperature. Solutions were then prepared by dissolving 150-200mg of the polymers in 1,2 dichloroethane, making the volume up to 10ml. and then diluting part of this solution to give solutions with polymer concentrations in the ratio 1: 2: 4: 8: The molecular weights were then determined by the method laid down in the instrument manual.

In order to calculate the molecular weights the instrument had to be calibrated using a compound with an accurately known molecular weight. A solution of benzil in 1,2 dichloroethane was prepared, diluted and measurements made in exactly the same way as for the polysulphone polymers.

3:17 ATTEMPTED CAPROLACTAM POLYMERISATION USING DIFFERENT COCATALYSTS.

Attempts were made to polymerise caprolactam at 150°C using sodium hydride as the catalyst and compounds which might act as cocatalysts. The compounds used were 4,4' dichlorodiphenyl sulphone, diphenylsulphone, 4,4' diamino diphenyl sulphone and diphenyl ether.

The required amount of caprolactam was weighed into a polymerisation tube and dried overnight in a vacuum oven at room temperature. The polymerisation tube was then fitted with a nitrogen bubbler and placed in a constant temperature bath. When all the caprolactam had melted approximately 2 mole % of the sodium hydride catalyst were weighed in in the usual way. When all the catalyst had reacted, shown to have taken place when bubbles of hydrogen ceased to be evolved, one of the compounds being examined as a cocatalyst was added. The amount added was approximately 0.6 mole %, more than sufficient to initiate polymerisation if the compound was a cocatalyst for the reaction. After two hours the polymerisation tube was removed from the constant temperature bath and its contents examined. The experiment was repeated for the remaining compounds.

3:18 COPOLYMER DENSITIES.

The densities of the copolymers were measured using a potassium carbonate solution-water density column with a density gradient of 1.1 to 1.3.

The marker floats which fell within the range of the column were cleaned and then placed in a sweep basket with the aid of tweezers. The sweep basket was then lowered gently to the bottom of the column using the sweep motor. The floats were checked to make sure no air bubbles were attached to them. After the floats had reached equilibrium, a minimum of 2 hours was necessary, their positions were determined with the aid of a cathetometer. The spheres were measured at their centre of volume and a graph of density versus cathetometer reading was plotted.

Three or four specimens were cut from each sample using a sharp scalpel. The cut edges were then checked to ensure that they were free from bits which might cause air bubbles to adhere to their surface. After the samples had been cleaned they were dropped gently into the column with the aid of tweezers. When the samples had reached equilibrium, a minimum of 2 hours was again required, their centres of volume were determined using a cathetometer. If there was a spread of results for a particular polymer other samples were tried to see if the spread was real or splurious. Air bubbles were found to be the most common source of error giving rise to low density values.

As the column was to be used more than once, the motorised unit was used to sweep out the floats and samples. Any attempt to withdraw the basket by hand would have resulted in the density gradient being disturbed.

3:19 SOLUTION PROPERTIES OF THE COPOLYMERS.

Attempts were made to dissolve samples of the copolymers, which had been extracted with water and chloroform, at room temperatures in pure solvents and mixtures of solvents. Shavings of the copolymers were weighed into a test tube, the required volume of solvent was added, and a ground glass stopper was fitted. The test tubes were gently shaken for 30 minutes on a mechanical shaker and the results observed. If the polymer had not dissolved it was shaken for a further period, overnight if necessary. Polymers which had not dissolved after shaking overnight were considered to be insoluble in that particular solvent.

Attempts were made to dissolve polycaprolactam and polysulphone in the solvents used for the copolymers.

3:110. THERMAL PROPERTIES OF THE COPOLYMERS.

The thermal properties of the copolymers were examined with the aid of a Du Pont 900 thermal analyser.

A sample of the copolymer, approximately 10mg.in weight was placed in an aluminium sample pan and covered with a lid. The pan was then placed on the sample position in the D.S.C. cell. The reference position contained an empty pan and lid. The sample and reference pans were always placed in position at room temperature. If the starting temperature was below room temperature the cell was cooled with liquid nitrogen. If the starting temperature was above room temperature the cell was heated at the experimental rate, the pen being set to record the results when the temperature was reached. A steady stream of nitrogen was passed through the cell during the course of the experiment. Increasing the temperature at a rate of 15°C per minute with a nitrogen flow rate of 0.3 litres per minute gave satisfactory results.

3:111 SPECTROSCOPY.

3:111.1 INFRA RED SPECTROSCOPY.

Infra red spectra were run on a Pye Unicam SP200G infra red spectrometer. The samples were in the form of films cast from solution.

3:111.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY.

N.M.R. spectra were run on a Perkin Elmar N.M.R. spectrometer using $CDCl_3$ and D_2O as solvents. This technique was used to analyse the water and chloroform soxhlet extraction products and the water insoluble part of the hydrolysis reaction.

3.112 OPTICAL MICROSCOPY.

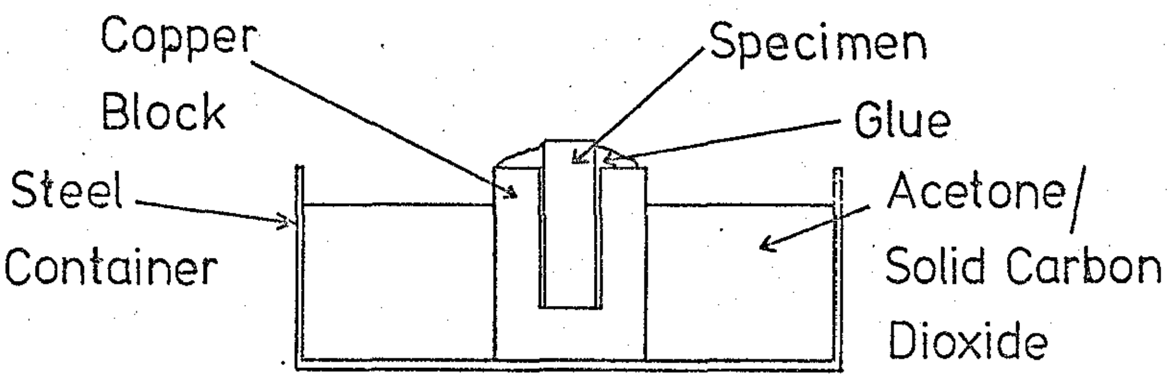
A standard sledge microtome was modified so that sections could be cut below room temperature. A cross section through the sample holder is shown in Figure 3a.

The specimen was parallelapiped in shape with a cross section similar to that shown in Figure 3b as this was found to make cutting easier. The original steel knife was replaced by a glass knife holder and a glass knife, the advantage of a glass knife being that it can easily be changed when the edge becomes dull.

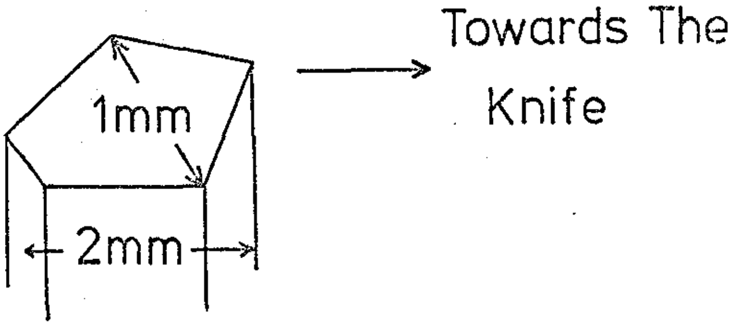
Cooling specimens well below their Tg is necessary to obtain thin sections, but overcooling must be avoided as it makes the specimens too brittle. For the copolymers it was found that an acetone/solid carbon dioxide bath cooled the specimens sufficiently to allow sections 2μ thick to be cut.

Once cut, a section was floated on the surface of a small bath of glycerol (because of its high surface tension) which was heated to about 100°C. This allows it to stretch and relax and eliminates deformations brought about by the cutting action. This treatment does of course have to be dispensed with if one is interested in the crystalline structure of the polymer. It is found that by taking a polymer above its Tg in this way modifies its crystalline structure. The sample was then washed in a small bath of distilled water and mounted on a glass slide beneath a cover slip using a commercial mounting oil with a refractive index of 1.53. The sections were transferred from one bath to the other using a loop of thin wire.

FIGURE 3

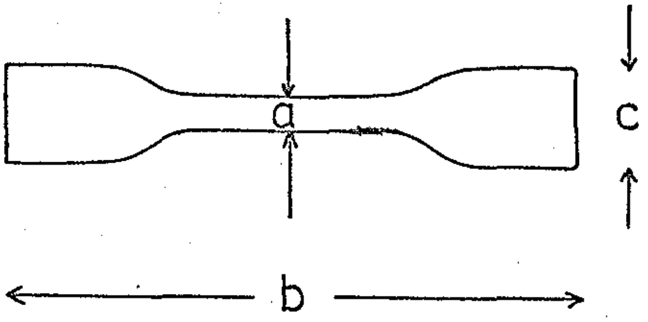


3a



3b

FIGURE 4



DIMENSIONS OF THE TEST PIECE

a = 4·0 mm

b = 76·0 mm

c = 12·0 mm

The prepared slides were examined using a Reichart Zetopan microscope fitted with a phase contrast condenser and objectives for transmitted light. This instrument enabled a microscopic examination of the sections up to a magnification of 1250 times. Photomicrography was possible using a KAM ES photomicrographic system. Several different areas of the sections were photographed at various magnifications for further detailed examination. The film used for the photomicrography was a fine grain negative film (Pan F) which was developed normally in Ilford ID 11, or, where high contrast was required, with Kodak D8 high contrast developer.

Assistance in this work was kindly provided by Mr. G. Ravioli.

3:113 PHYSICAL PROPERTIES OF THE COPOLYMERS.

3.113.1 MOULDING THE COPOLYMERS.

The polysulphone-polycaprolactam copolymers were compression moulded in an electrically heated press (Moore 20 ton press) fitted with water cooling. Two moulds were used, one which gave a "sheet" from which tensile specimens could be cut, and one which gave a "slab" from which impact specimens could be cut. The mould sizes were 6" x 6" x 0.06" and 6" x 2" x 0.2" respectively. The samples were moulded between stainless steel plates. Aluminium plates were placed between the stainless steel plates and the platens of the press to prevent the latter from being damaged. The stainless steel plates were coated with a P.T.F.E. spray just before use and this acted as a mould release agent.

The press was heated to the required temperature which was between 230 and 245°C, depending on the polymer being moulded. It was found that a higher temperature was needed as the amount of polysulphone in the copolymer was increased. The polymers obtained from the polymerisation tubes were cylindrical, and as such unsuitable for moulding. If the polymer was to be moulded into a "sheet" from which tensile specimens were to be cut it was turned on a lathe to give shavings which were used to fill the mould. If the polymer was to be moulded into a "slab" from which impact specimens were to be cut, the polymer was cut into pieces with a saw. The amount of polymer required for the tensile and impact specimen moulds was 15 and 12.5 gms respectively.

The mould was assembled, filled with polymer, and then placed on the lower platten of the press which had been preheated to the required temperature. The press was closed until the top set of plates were in contact with the top platten of the press. As the polymer melted the press was closed at such a rate that both sets of plates were in contact with the plattens all the time. When the mould was first placed in the press the temperature of the plattens dropped by about 10°C. When the temperature of the plattens had returned to the moulding temperature and the polymer had completely melted the mould was closed to a pressure of 20 tons. The moulding time for all polymers was 10 minutes. After the prescribed length of time the heating was turned off and the plattens cooled. The mould was removed from the press when the temperature of the plattens had dropped to below 100°C.

The "sheets" from which tensile specimens were cut had good surface finishes and were free from sink marks. When polymers were moulded into "slabs" from which impact specimens could be cut,care had to be taken to ensure that when they melted they flowed and filled the mould. If this was not achieved the "slabs" contained holes and sink marks. In all cases the "slabs" had good surface finishes.

3:113.2 TENSILE STRESS-STRAIN MEASUREMENTS.

Tests were made on dumbell test pieces (Figure 4) which were cut from compression moulded sheets using a die punch cutter.

The tensile and elongation properties of the copolymers were studied in a constant temperature room (23° ± 0.5°C, 65% RH).

An Instron Universal Testing Tensometer (Model TT-CM) fitted with a CTM load cell, was used to measure the tensile properties of the copolymers. The instrument was fitted with pneumatic jaws, the pressure on which was set to prevent sample slippage, but at the same time keep jaw breaks to a minimum.

Before any of the samples were tested the instrument was calibrated by the method laid down in the manual. Each test piece was then measured for thickness, to 1 x 10^{-5}m, using a micrometer. These measurements were made about the portion to be tested and the results averaged.

Two lines, 0.5 inches apart, were marked on the middle of the portion to be tested. The specimen was then inserted centrally into the pneumatic jaws and the jaws closed. The instrument was started and the test commenced. The following test conditions were used.

TEST SPEED	0.05m/minute
INITIAL JAW SEPARATION	0.04m
CHART SPEED	0.05m/minute
TEST TEMPERATURE	$23^{\circ} \pm 0.5^{\circ}C$
FULL SCALE DEFLECTION	20 or 50 kg.

The test was continued until the sample broke. The way in which the sample elongated was observed throughout the test. During the test the distance between the marks on the test portion was followed and the distance between them when the sample broke was recorded. This was achieved by holding a stiff piece of paper, graduated in 0.1 ins, alongside the specimen as it was being tested.

3:113.3 CHARPY IMPACT TEST.

The impact strengths of the copolymers were determined using the Hounsfield Impact testing machine. The machine consists of a means of supporting the test pieces and a calibrated pendulum or "tup". The machine will accept a series of interchangeable tups which cover the range of impact strengths likely to be tested. The energy stored in the tups varies from 2lb. down to 1/32lb. The energy of fracture is equal to the initial energy stored in the tup, less the energy remaining after impact.

Test specimens $\frac{1}{4}$ inch in depth were cut from the compression moulded "slabs" and a standard notch was cut into each sample using a Hounsfield notching machine. The thickness of the sample behind the notch was measured using a micrometer.

The sample was placed in position on the machine and the tup raised. The tup was chosen to give a residual energy reading between 35 and 70% of the initial energy. The tup was allowed to fall and strike the sample, the residual energy being recorded. Occasionally a sample did not break cleanly and when this happened the sample was discarded. After testing, the depth of the sample behind the notch was measured.

3:114 BRABENDER PLASTOGRAPH.

Commercial nylon 6 and polysulphone were mixed in a Brabender plastograph. The machine was heated by pumping hot oil through the jaws, one of which contained the mixing screws which rotated in the opposite direction. The two polymers were mixed at 240°C for various times. It was found that after about 10 minutes the nylon 6 started to degrade even when the mixing chamber was flushed out with nitrogen prior to mixing. After the polymers had been mixed for a prescribed length of time, which was not more than 10 minutes, the machine was stopped and the blended polymers quickly removed. The polymer blends were compression moulded into "sheets" from which tensile test pieces were cut.

3:2 RESULTS AND DISCUSSION.

3:21 COPOLYMER COMPOSITION.

The effect of time and catalyst concentration on the polymerisation of caprolactam in the presence of dissolved polysulphone was studied. Three series of copolymers were prepared, each containing 10% by weight of polysulphone, with polymerisation times of 1,2 and 4 hours respectively. For each series copolymers were prepared using various catalyst concentrations.

It was ssumed that the amount of polysulphone lost during the polymerisation was negligible so that when the weight of the final polymer was known the percentage of polysulphone in it could be calculated. For each copolymer the amount of caprolactam converted to polymer was determined by extracting shavings of the copolymer with water for 24 hours in a soxhlet extraction apparatus. Knowing the amount of polysulphone in each copolymer it was possible to calculate the percentage monomer converted to polymer. The results, given in Tables 11-13, are the average of at least two determinations and were found to be consistent to within 1%. They are illustrated in Figures 5-7.

After the shavings had been extracted with water they were extracted for three days in a soxhlet extraction apparatus using chloroform as the solvent. Any free polysulphone was extracted so that, knowing the original weight of polysulphone in the shavings, the amount combined with the polycaprolactam could be calculated.

COPOLYMER COMPOSITION : POLYMERISATION TIME 1 HOUR

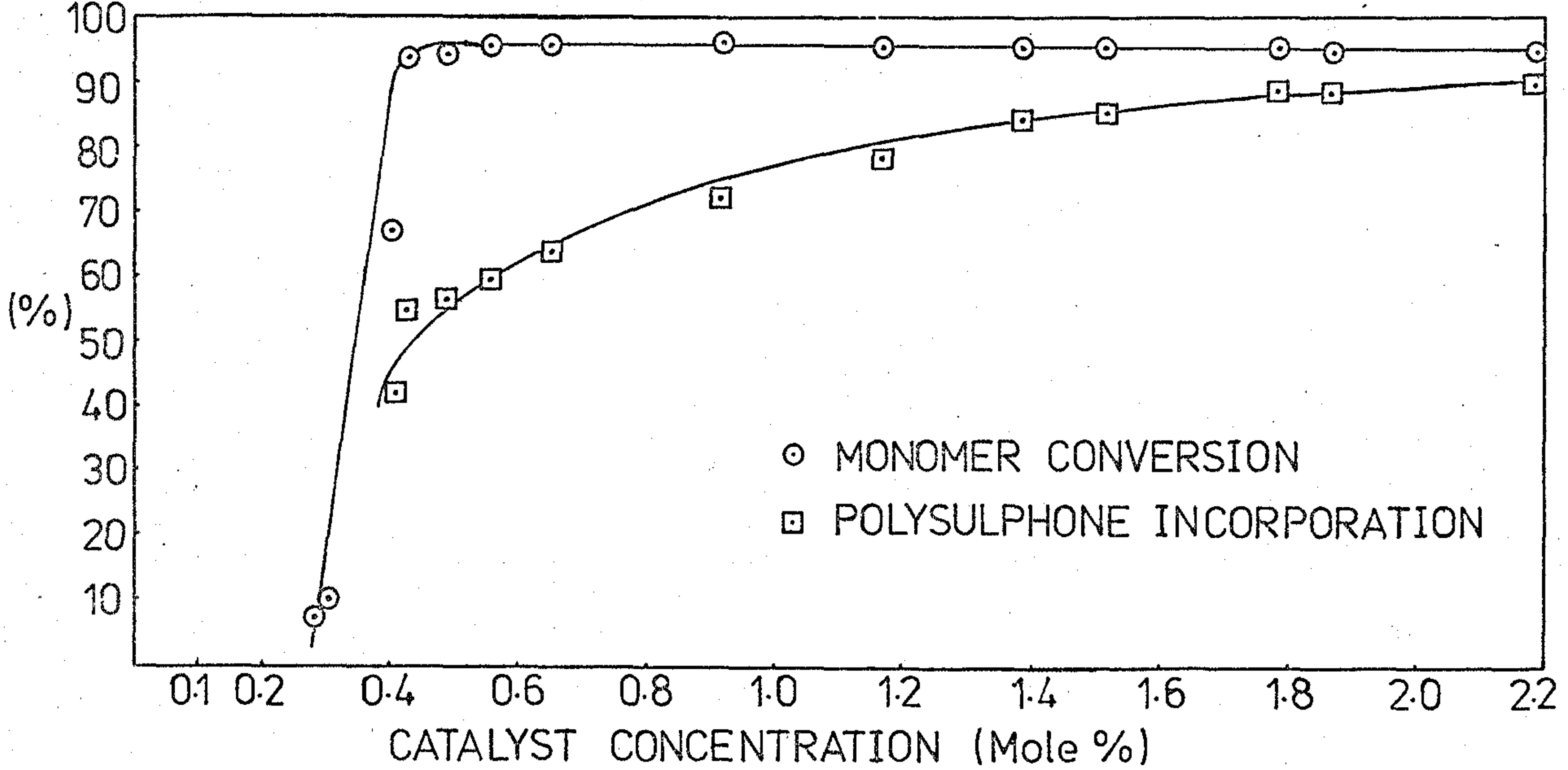


FIGURE 5

COPOLYMER COMPOSITION: POLYMERISATION TIME 2 HOURS

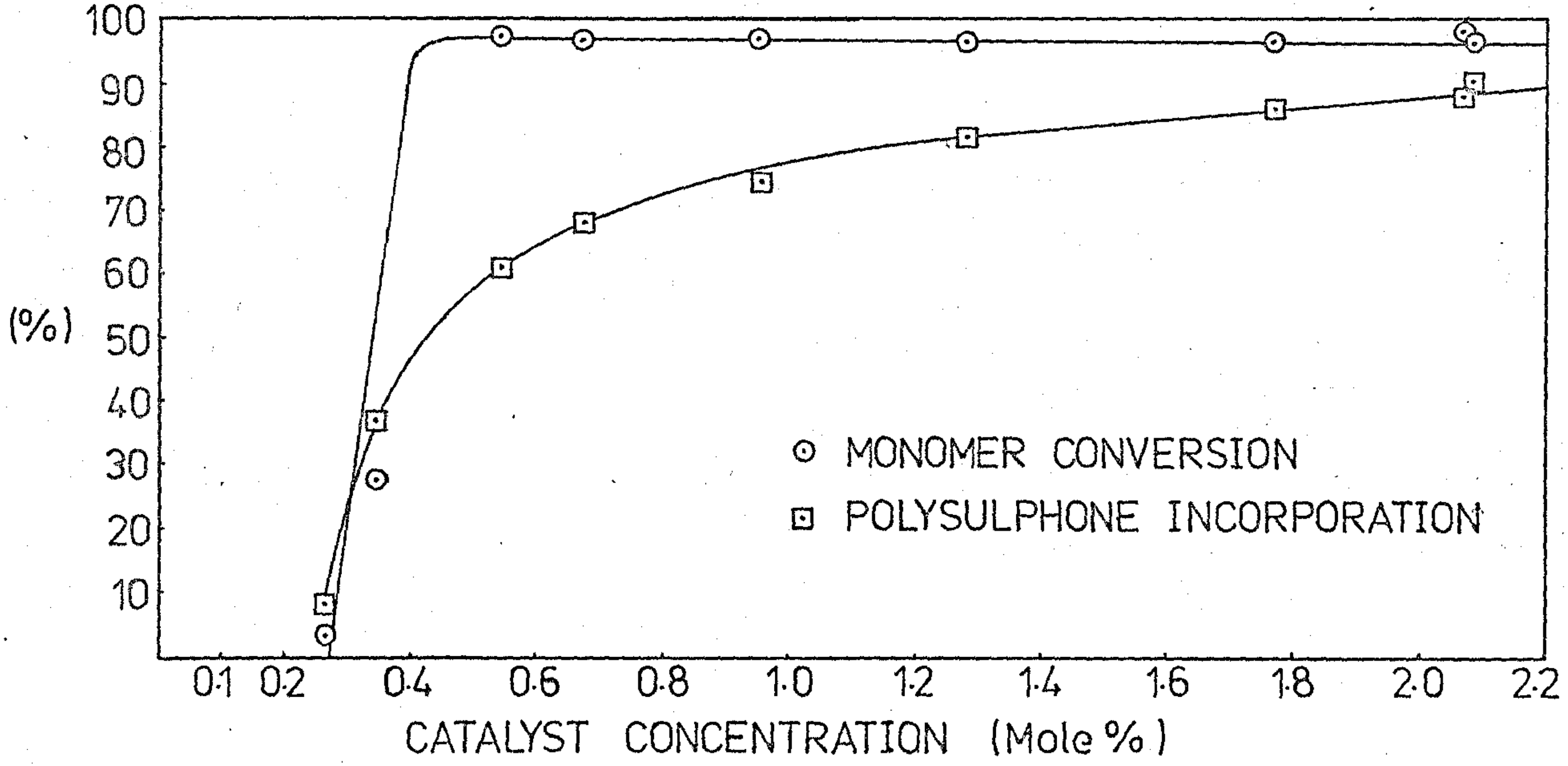


FIGURE 6

COPOLYMER COMPOSITION: POLYMERISATION TIME 4HOURS

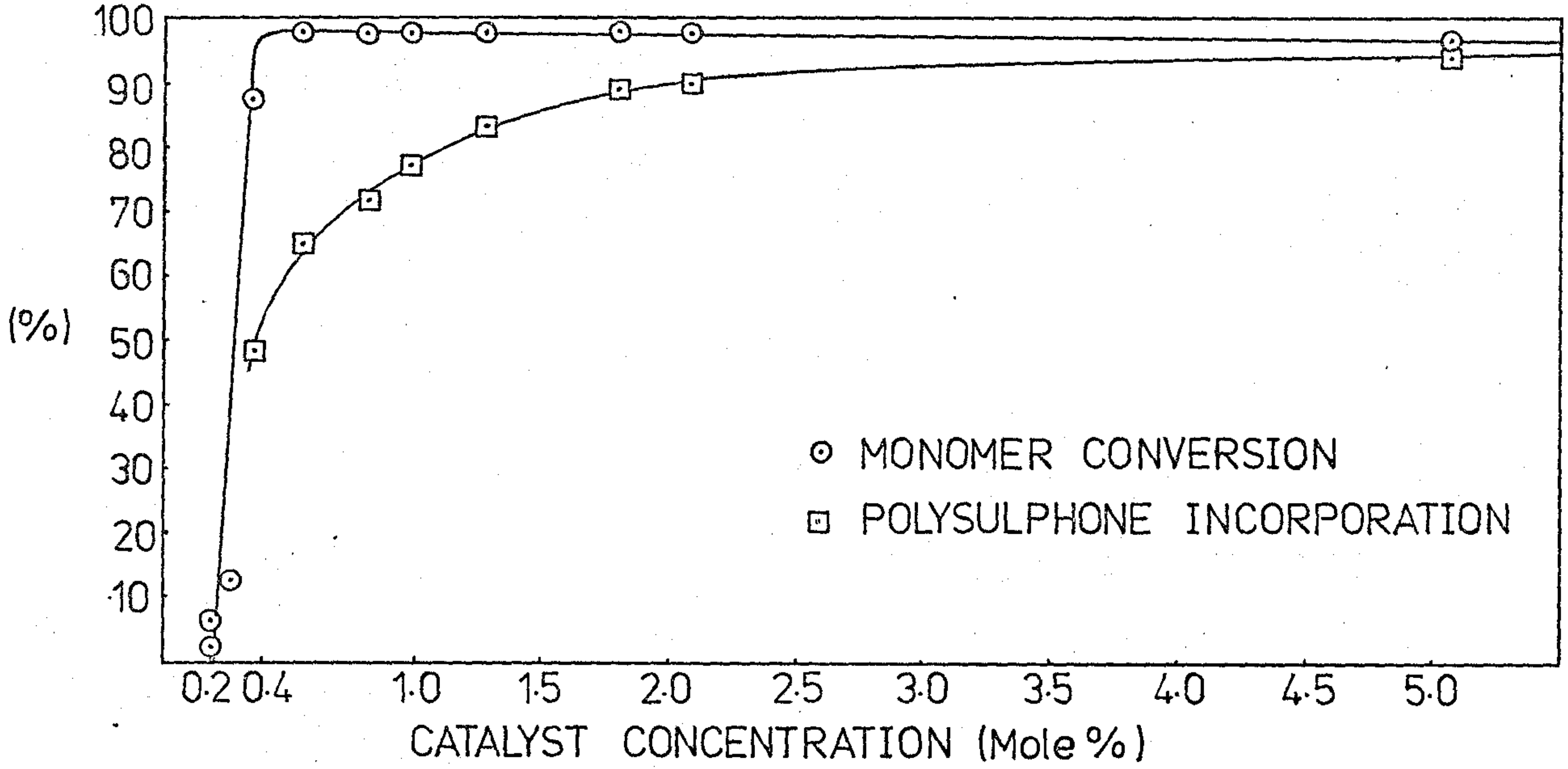
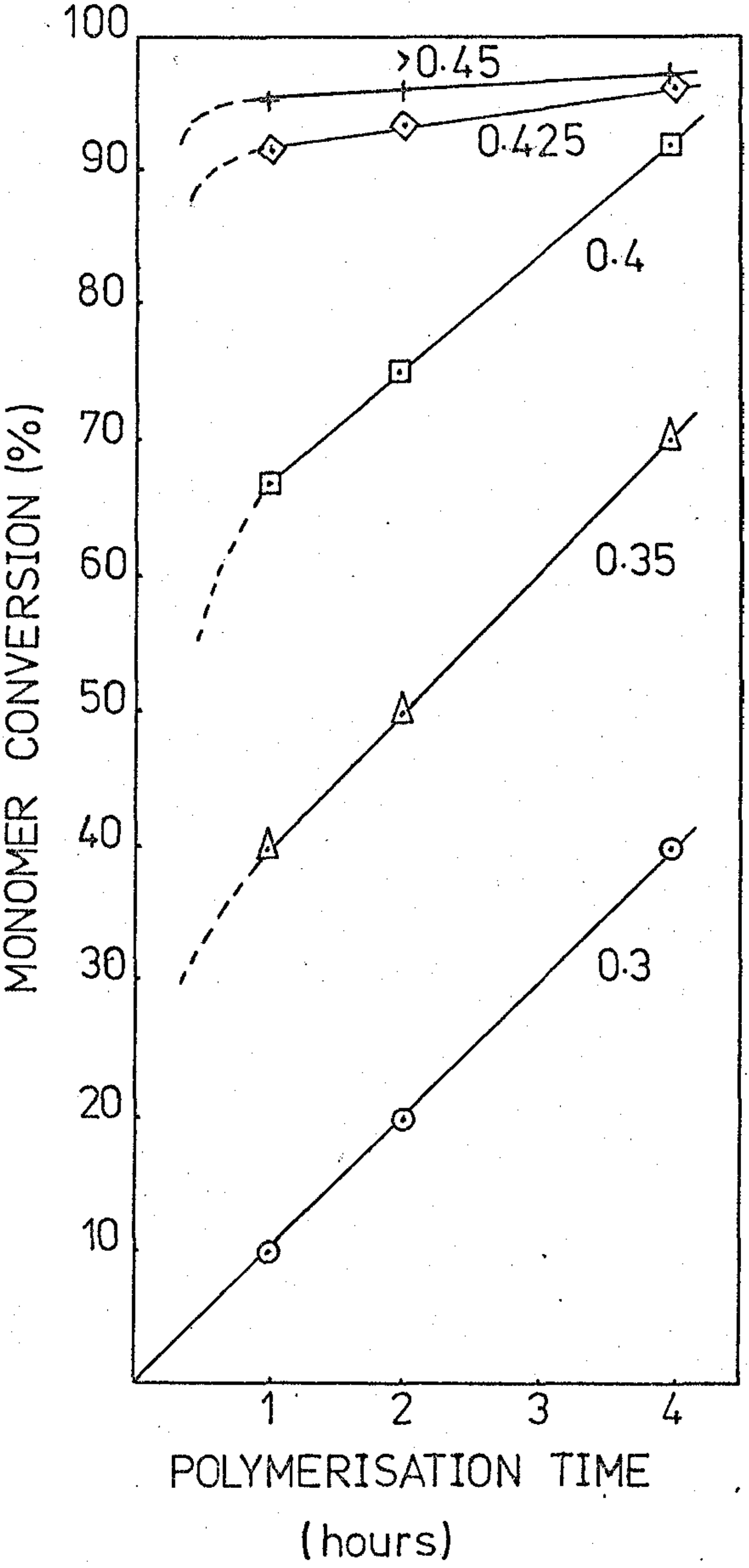


FIGURE 7

FIGURE 8



MONOMER CONVERSION WITH TIME AND CATALYST CONCENTRATION

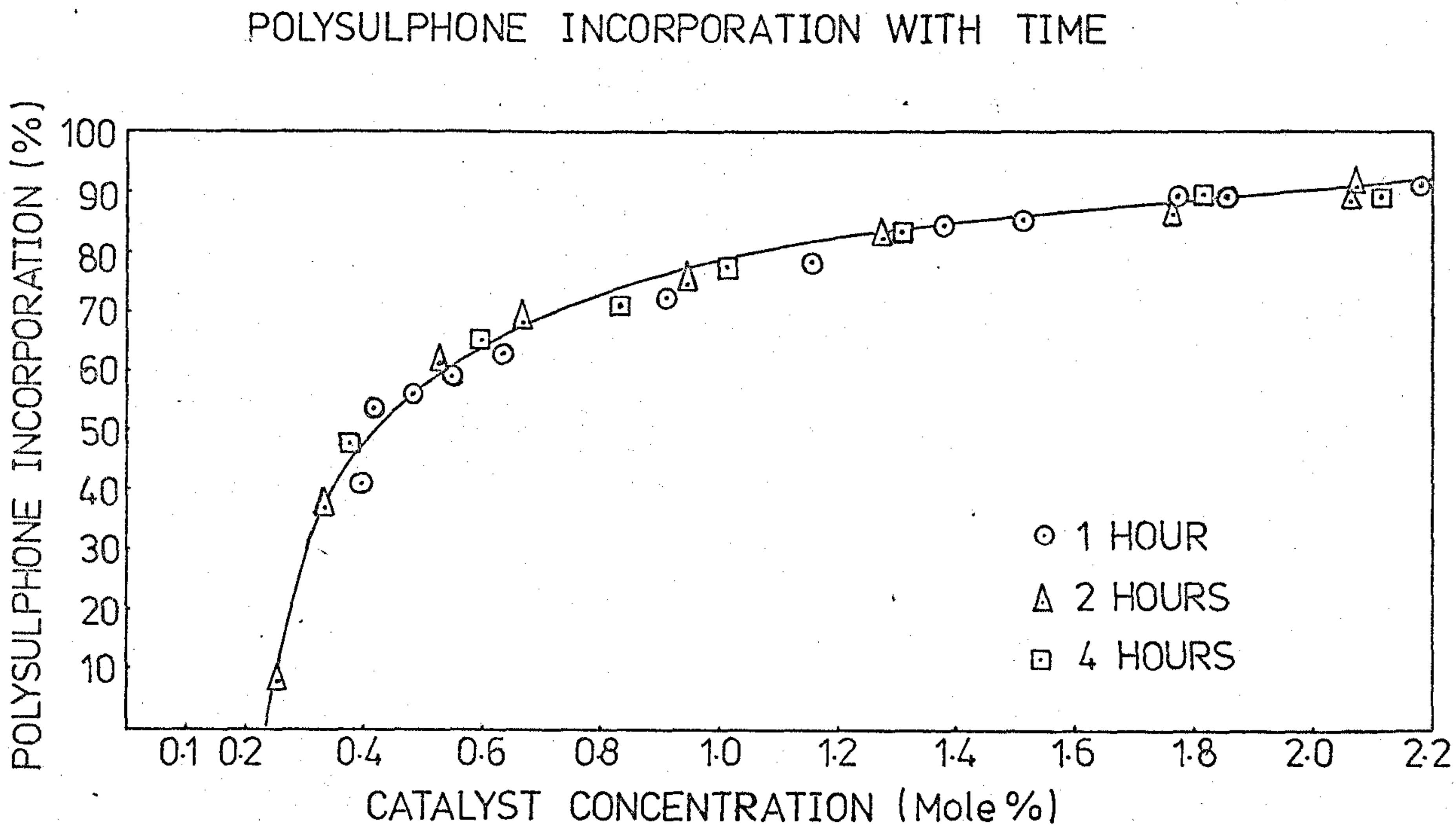

POLYSULPHONE INCORPORATION WITH TIME
POLYSULPHONE INCORPORATION (%)
100
90
80
70
60
50
40
30
20
10
0·1
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
CATALYST CONCENTRATION (Mole %)
⊙ 1 HOUR
Δ 2 HOURS
⊡ 4 HOURS

FIGURE 9

The results, the average of at least two determinations, are given in Tables 11-13 and are consistent within a few percent. They are illustrated in Figures 5-7. The data is as measured, the consistency of any one determination being approximately ± 0.5%, hence the determination of the amount of polysulphone attached to the polycaprolactam can only be accurate to within ± 2.5%.

Figure 8 shows the conversion of monomer to polymer with time for various catalyst concentrations. Figure 9 shows the percentage of the original polysulphone attached to the polycaprolactam as the catalyst concentration is increased for the various polymerisation times.

3:21.1 MONOMER CONVERSION.

Figures 5-7 show the conversion of monomer to polymer at various catalyst concentrations for polymerisation times of 1,2 and 4 hours respectively. The curves are typical for caprolactam polymerisation using a catalyst and a cocatalyst. At very low catalyst concentrations, below 0.15 mole %, no polymerisation occurs because degradation reactions destroy all the catalyst and lactam anions formed.

TABLE 11.

POLYCAPROLACTAM-POLYSULPHONE COPOLYMERS.

B SERIES: POLYMERISATION TIME 1 HOUR.

No.	CATALYST CONCENTRATION (MOLE %)	% POLYSULPHONE IN FINAL POLYMER.	% MONOMER CONVERTED TO POLYMER	%POLYSULPHONE ATTACHED TO POLYCAPROLACTAM
B1	1.78	10.03	95.73	89
B2	1.86	9.97	95.41	89
B3	0.28	10.06	6.50	-
B4	0.30	10.05	9.50	-
B5	0.40	10.05	66.67	41
B6	1.38	9.98	95.73	84
B7	0.91	9.93	95.81	72
B8	0.55	9.98	95.56	59
B9	0.48	10.04	94.39	56
B10	1.16	10.01	95.60	78
B11	0.42	10.12	93.56	54
B12	1.51	10.03	95.56	85
B13	2.19	10.06	95.58	91
B14	0.64	9.97	95.44	63

TABLE 12.

POLYCAPROLACTAM - POLYSULPHONE COPOLYMERS.

C SERIES: POLYMERISATION TIME 2 HOURS.

No.	CATALYST CONCENTRATION (MOLE %)	% POLYSULPHONE IN FINAL POLYMER	% MONOMER CONVERTED TO POLYMER	% POLYSULPHONE ATTACHED TO POLYCAPROLACTAM.
C1	0.67	10.13	96.83	68
C2	1.28	9.90	96.70	82
C3	0.34	9.97	27.46	37
C4	0.95	10.16	96.73	74
C5	2.07	10.14	97.63	88
C6	2.08	10.09	96.41	90
C7	1.77	10.12	96.58	86
C8	0.54	10.02	96.69	61
C9	0.26	10.41	2.95	8

TABLE 13.

POLYCAPROLACTAM - POLYSULPHONE COPOLYMERS.

D SERIES: POLYMERISATION TIME 4 HOURS.

N°.	CATALYST CONCENTRATION (MOLE %)	% POLYSULPHONE IN FINAL POLYMER	% MONOMER CONVERTED TO POLYMER	% POLYSULPHONE ATTACHED TO POLYCAPROLACTAM.
D1	2.12	10.24	97.73	89
D2	1.02	10.10	97.93	77
D3	1.31	10.08	97.41	83
D4	0.60	10.14	97.58	65
D5	0.38	10.40	87.22	48
D6	0.20	10.12	1.67	-
D7	1.82	10.15	97.38	89
D8	0.84	10.08	97.48	71
D9	0.28	9.98	18.39	-
D10	0.21	10.19	6.73	-
D11	5.11	10.09	95.34	94

For catalyst concentrations between 0.15 and 0.25 mole % there is a small but gradual increase in the conversion of monomer which is especially noticeable for the D series where the polymerisation time is 4 hours. For catalyst concentrations between 0.25 and 0.6 mole % the conversion of monomer rises rapidly to 90% and then more slowly to a limiting value, constant within 1% for each series, and dependent on the polymerisation time. The values are 95.5 ± 0.5, 96.5 ± 0.5 and 98.0 ± 0.5% for polymerisation times, 1, 2 and 4 hours respectively. In this range of catalyst concentrations more lactam anions are formed which initiate more polymer chains with a resultant increase in the conversion of monomer to polymer. For catalyst concentrations between 0.6 and 2.5 mole % the conversion of monomer to polymer remains constant for each series, the values being those given above.

A polymer was prepared with a catalyst concentration of 5 mole % and a polymerisation time of 4 hours. At this very high catalyst concentration there is a decrease in the conversion of monomer to polymer but this is readily explained in terms of degradation reactions which are the same as those which occur in normal lactam polymerisation by an anionic mechanism (page 217).

Figure 8 illustrates the conversion of monomer to polymer with time for various catalyst concentrations. At catalyst concentrations between 0.2 and 0.5 mole % monomer conversion is highly dependent on the concentration and on the polymerisation time. Increases in the catalyst concentration above 0.5 mole % results in only a small increase in monomer conversion. The polymers will contain little monomer but there will be changes in the molecular weight distribution.of the polycaprolactam components of the copolymers.

3:21.2 AMOUNT OF POLYSULPHONE ATTACHED TO POLYCAPROLACTAM.

It is possible to calculate the amount of polysulphone attached to the polycaprolactam in the copolymers by extracting any uncombined polymer with chloroform. Figures 5-7 show the amount of polysulphone attached to polycaprolactam at various catalyst concentrations for polymerisation times of 1,2 and 4 hours respectively. Because of the small differences in weight involved the errors are greater than for the monomer conversion experiments and this accounts for the scatter of points on the curve. Even with catalyst concentrations as high as 5 mole % there is still almost 6% uncombined polysulphone in the polymer.

The tangential nature of the curves shows that there can never be 100% incorporation and is indicative of a chain scission reaction. Figure 9 indicates that the curves are superimpossible which means that, as in the normal anionic polymerisation of caprolactam, the reaction is controlled by the catalyst concentration. For the polymerisation times considered the percentage of polysulphone attached to polycaprolactam is independent of time. Support for these conclusions is provided by the results of the experiments to determine the reaction mechanism.

From these results it was decided to prepare copolymers to the specifications given in Table 14.

3.22 COPOLYMER COMPOSITION AND REACTION MECHANISM.

Polycaprolactam-polysulphone copolymers were prepared to study the effect of catalyst concentration and polysulphone content on copolymer composition and some physical properties of the copolymers. The polymerisation time was two hours and the polymers were prepared to the specifications given in Table 14.

TABLE 14.

SERIES.	% POLYSULPHONE IN POLYMER	CATALYST CONCENTRATION (MOLE %)
E	5 ± 0.05	1 ± 0.05
H	5 ± 0.05	2 ± 0.05
F	10 ± 0.05	1 ± 0.05
J	10 ± 0.05	2 ± 0.05
G	15 ± 0.08	1 ± 0.08
K*	10 ± 0.05	1 ± 0.05

*Prepared using polysulphone with a higher molecular weight.

For each series sufficient copolymers were prepared under the above conditions in order that some of their physical properties could be measured and their composition determined. Two polymers from each series were chosen at random in order to determine their composition, measure the molecular weight of the polysulphone attached to the polycaprolactam and to study other properties to be discussed later. The remainder were subjected to physical testing. Details of all the copolymers prepared, and to which test each was subjected are given in Appendix 2.

Caprolactam polymerisation was attempted with sodium hydride as the catalyst and other compounds which might act as cocatalysts. It was hoped that the results from these attempted polymerisations, together with the results of the copolymer composition experiments, a reaction mechanism could be proposed.

3:22.1 COPOLYMER COMPOSITION.

The copolymers were extracted with water and chloroform to remove any unreacted monomer and uncombined polysulphone respectively. The results of the extraction experiments are given in Table 15. It was found that if the polysulphone content was 5% extraction with chloroform would remove little, if any, uncombined polysulphone. This can be explained in terms of the phase structure of the copolymers and is discussed in more detail in the section of optical microscopy. For polymers prepared with 5% polysulphone the uncombined polysulphone was removed by extracting reprecipitated copolymers with chloroform.

The extraction products were analysed by infra-red and N.M.R. spectroscopy. By comparing the curves with those for caprolactam and polysulphone it is clear that the separations were clean and satisfactory.

3:22.2 MONOMER CONVERSION .

The results show that it is possible to make accurate determinations of monomer conversion whatever the catalyst concentration or polysulphone content of the copolymers.

TABLE 15.

POLYCAPROLACTAM- POLYSULPHONE COPOLYMERS

COPOLYMER COMPOSITION.

N°.	CATALYST CONC. (MOLE %)	POLYSULPHONE IN FINAL POLYMER (%)	CONVERSION OF MONOMER TO POLYMER (%)	POLYSULPHONE COMBINED WITH POLYCAPROLACTAM (%)
E1	1.01	4.99	96.99	82
E8	0.98	5.02	97.12	84
H7	2.00	5.03	96.18	91
H12	2.01	4.99	96.29	93
F10	0.97	10.00	97.05	76
F13	0.97	9.99	96.83	75
J8	1.99	10.02	96.27	88
J9	1.98	9.99	96.20	89
G2	1.00	14.93	96.90	63
G9	1.01	15.00	96.83	61
K1	0.99	9.99	97.03	78
K2	1.01	10.02	97.05	79

For all the copolymers the results were consistent to within 1%. If the values for the copolymers prepared with 10% polysulphone were to be plotted on Figure 6 they would lie exactly on the curve.

3:22.3 AMOUNT OF POLYSULPHONE COMBINED WITH POLYCAPROLACTAM.

For the polymers containing 10 and 15% polysulphone the amount of polysulphone combined with polycaprolactam can be determined by extracting shavings of the polymer with chloroform. The values cannot be determined with the same accuracy as for the monomer conversion because of the small differences in weights involved. The average of three determinations was considered to give accurate results. If the values for the polymers prepared with 10% polysulphone were to be plotted on Figure 6 they would lie close to the curve. When polymers are prepared with only 5% polysulphone it is impossible to extract any uncombined polysulphone by simple chloroform extraction, The polymers had to be reprecipitated in order to produce a structure which allows chloroform to extract the uncombined polysulphone. There is a change in the phase structure of the copolymers as the polysulphone concentration is increased from 5 to 10% by weight.

3:22.4 HYDROLYSIS OF THE COPOLYMERS.

The extracted copolymers were hydrolysed by refluxing for fourty hours with a solution of hydrochloric acid. It has been shown [108,109] that nylon 6 is almost completely hydrolysed by this solution to ϵ aminocaprionic acid hydrochloride which is water soluble. If the molecular weight of the polysulphone segments in the copolymers are to be measured it is essential that they are not affected by the hydrolysing solution. Polysulphone was refluxed with hydrochloric acid for fourty hours and recovered unaffected.

After the copolymers had been hydrolysed the insoluble part was filtered off, reprecipitated from chloroform and analysed. Infra red and N.M.R. spectroscopy and differential thermal analysis showed it to be pure polysulphone. The water soluble part was recovered by evaporation and its melting point was determined by thermal analysis. The melting point of the product was 125-127°C and the literature melting point of ε Amino caprioic acid hydrochloride is 122°C.

Hydrolysis of the copolymers gave two products, a water soluble one and one that is insoluble in water. The analysis of the water insoluble part of the hydrolysis product showed it to be pure polysulphone. None of the analytical techniques used were able to detect the presence of polycaprolactam. The molecular weights determined are therefore the molecular weights of the polysulphone combined with polycaprolactam in the copolymers.

No attempt was made to recrystallise the water soluble part of the hydrolysis product. The melting point of the product obtained was considered to be sufficiently close to the literature value of ε amino caprioic acid hydrochloride for it to be that compound.

3:22.5 MOLECULAR WEIGHT DETERMINATION.

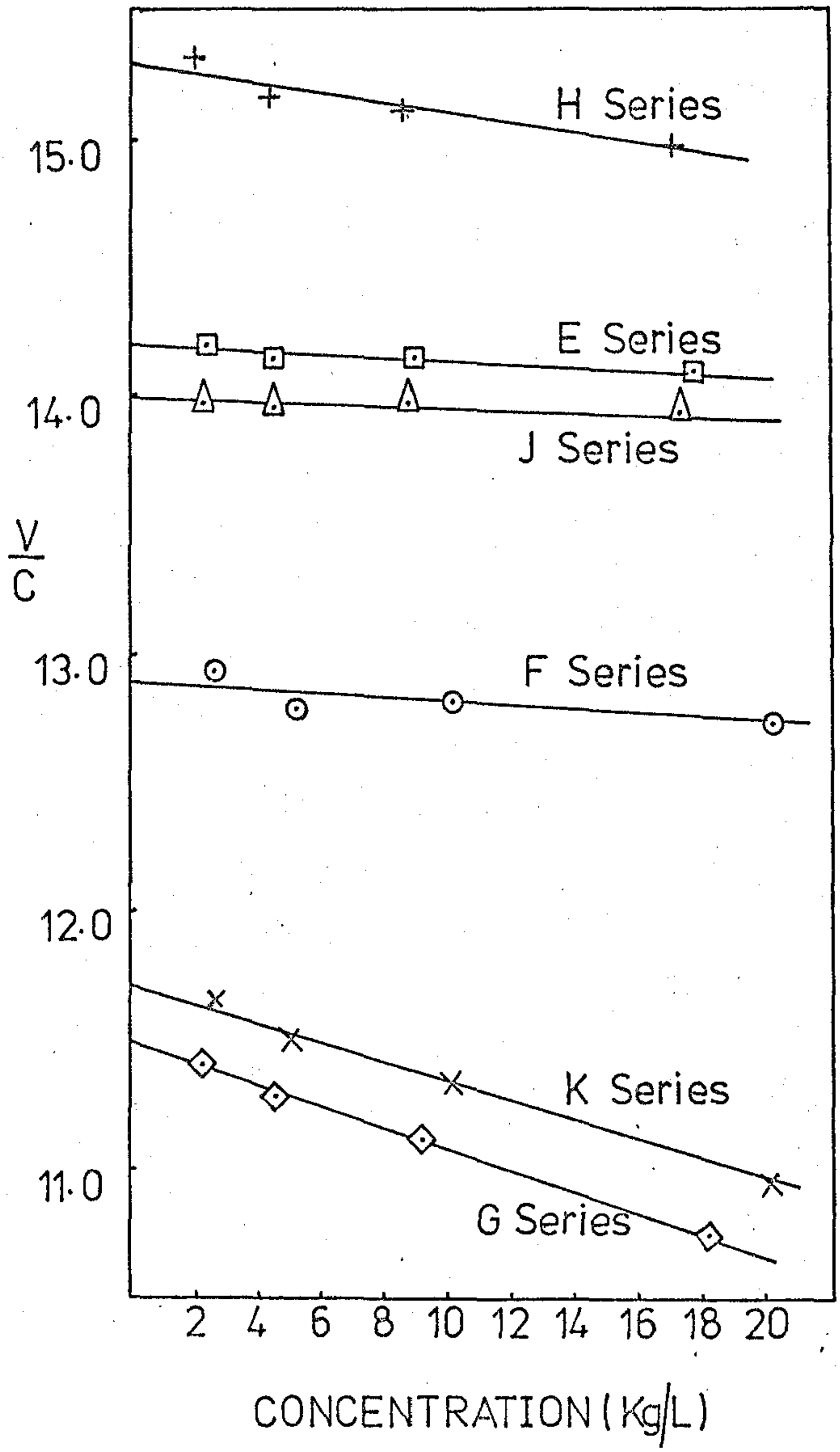
The molecular weights of the polysulphone polymers from the hydrolysed copolymers were determined by vapour pressure osmometry. Plots of $^V/C$ v C, where V is the bridge output voltage and C is the concentration are shown in Figure 10. The molecular weight is given by the following equation.

$$M_N = \frac{K}{\left(\frac{V}{C}\right)_{C \to 0}} \quad \text{------} \; (20)$$

where M_N is the number average molecular weight
K is the calibration factor.

FIGURE 10

A GRAPH OF $^{V}/_{cvc}$ FOR MOLECULAR WEIGHT DETERMINATION



Benzil, a compound with an accurately known molecular weight was used as the calibration standard, and gave a value of 16,080 for the calibration constant. The molecular weights of the polysulphone polymers have been calculated from equation 20 and listed in Table 16.

TABLE 16.

MOLECULAR WEIGHTS OF THE POLYSULPHONE COMPONENTS OF THE COPOLYMERS.

SERIES.	% POLYSULPHONE IN ORIGINAL POLYMER.	MOLECULAR WEIGHT (M_N)	AVERAGE NUMBER OF POLYSULPHONE UNITS
E	5	1148	2.60
H		1047	2.37
F	10	1247	2.82
J		1128	2.55
G	15	1398	3.16
K	10	1374	3.11

The importance of these results is that they confirm that chain scission of the polysulphone molecules occurs during the polymerisation, a feature which must be explained by any proposed reaction mechanism. The results of the copolymer composition experiments had suggested that the polysulphone molecule was broken during the polymerisation but these results were needed in order to prove it. The low molecular weights of the polysulphone fragments indicates that the polymer is an efficient cocatalyst for the anionic polymerisation of caprolactam. As expected, an increase in the catalyst concentration resulted in a decrease in the molecular weight of the polysulphone fragments. Also, the molecular weight increases as the polysulphone concentration is increased. Although at first the values seem to be very similar the differences between them are of the right order of magnitude, taking into consideration the results of the copolymer composition experiments.

From the results it is also possible to make some comments on the structure of the copolymers. It would appear that the copolymer molecules consist of long chains of polycaprolactam with one, and possibly more, low molecular weight polysulphone fragments attached to them. It was hoped that the experiments with the attempted alternative cocatalysts would make it possible to propose a reaction mechanism and to determine whether block or graft copolymers are formed.

These results will be referred to again in the discussion of the copolymer density results and the photographs in the section on optical microscopy.

3:22.6 ATTEMPTED ALTERNATIVE COCATALYSTS.

As polysulphone acts as a cocatalyst in the polymerisation of caprolactam,attempts were made to polymerise the monomer using compounds which might act as cocatalysts. The compounds tried were small molecules which resembled parts of the polysulphone molecule and gave the following results.

When 4,4' dichlorodiphenyl sulphone was added to caprolactam containing lactam anions polymerisation occured. The colourless solution turned white as the polycaprolactam started to crystallise. After a time, which depended on the cocatalyst concentration, the colour of the polymer changed from white, through yellow and orange, to red. When shavings of the polymer were exposed to air and moisture their colour changed from red to white.

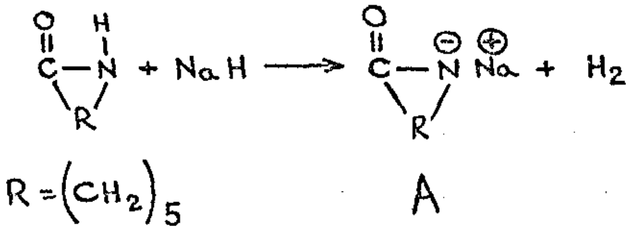
When diphenyl sulphone was added to a solution of lactam anions no change in the viscosity of the solution was observed to have taken place after two hours at 150°C. Extraction with water showed that no polymerisation had taken place.

4,4' diaminodiphenyl sulphone did not act as a cocatalyst in the polymerisation of caprolactam. When the contents of the polymerisation tube were examined it was found that no polymer had been formed.

Diphenyl ether, when added to caprolactam containing lactam anions, failed to initiate polymerisation after two hours at 150°C. When sodium hydride was added to a solution of caprolactam containing diphenyl ether the solution turned bright red but polymerisation did not occur.

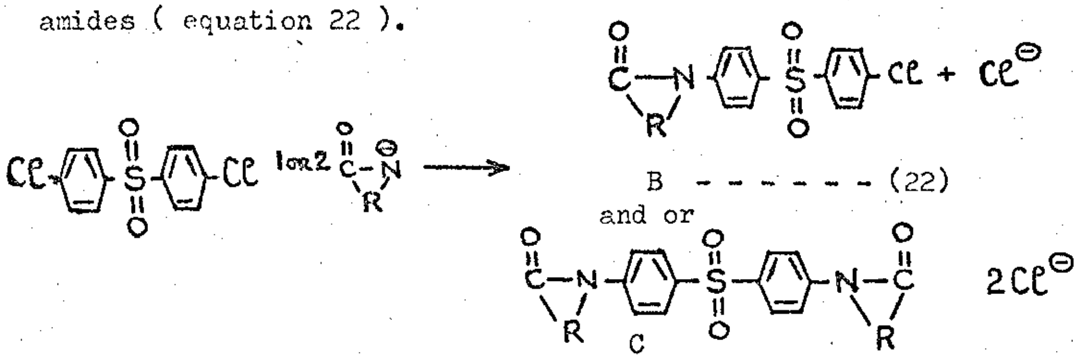
Of the compounds tried as alternative cocatalysts in the anionic polymerisation of caprolactam only 4,4' dichlorodiphenyl sulphone initiated polymerisation. A reaction mechanism is proposed which agrees with other work[71] published subsequent to the present study. It explains why 4,4' dichlorodiphenyl sulphone initiates polymerisation and why other compounds tried do not.

The first step, as in the anionic polymerisation of caprolactam, is the formation of lactam anions A by the reaction of the monomer with sodium hydride (equation 21).



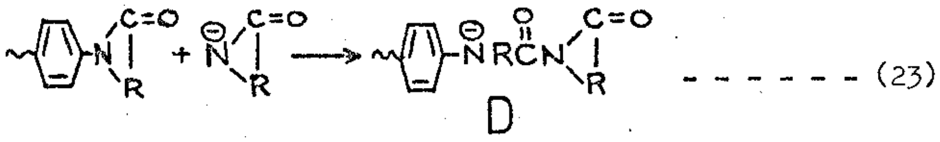
- - - - - - (21)

When the 4,4' diphenyl sulphone cocatalyst is added it reacts with the lactam anions with the formation of mono and difunctional amides (equation 22).



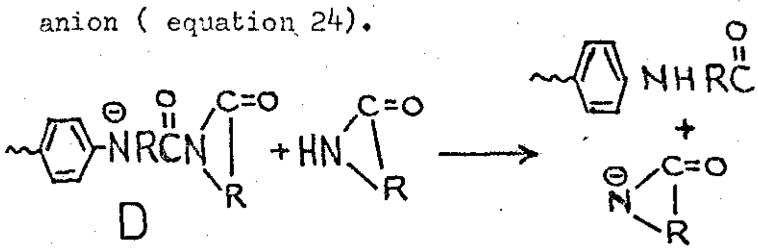
At lower catalyst concentrations it would be expected that more monofunctional amide would be formed. With chlorine the inductive and mesomeric effects are in opposite directions but the overall effect is that chlorine is an electron withdrawing group. The electron withdrawing chlorine atoms have a higher electron density than the carbon atoms in the 4 and 4' positions and this makes them labile to nucleophilic attack.

The difunctional amide C, due to the strongly electron arylene group attached to the amide nitrogen is extremely labile to base and undergoes very facile ring opening reactions (equation 23).



The sensitivity to base of compound C is such that it has eluded all attempts at isolation.[71] Instead, high molecular weight polymer always resulted whenever free caprolactam monomer was present in the system. The formation of C is slow and determines the rate of reaction, once it is formed polymerisation is very rapid.

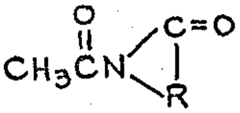
Anion D, being more basic than a caprolactam molecule, abstracts a hydrogen atom from the monomer and reforms a lactam anion (equation 24).



------(24)

Caprolactam polymerisation then proceeds with transamidation by lactam anion, followed by hydrogen abstraction as described in the mechanism of the anionic polymerisation of caprolactam (Appendix 1).

Compound C is analagons to the same class of imides as N-acetyl caprolactam E



E

It can be seen that both A and E possess a carbonyl group within a lactam ring which is activated towards attack by lactam anion. This activation is a function of the electron withdrawing power of the group attached to the nitrogen atom, and this sensitivity to base is why both act as cocatalysts in the anionic polymerisation of caprolactam.

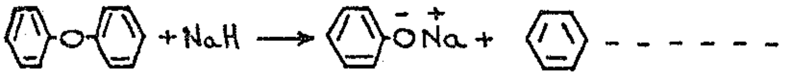
Other activated aromatic halides which initiate polymerisation have also been investigated by Matzner.[71] His results show that there is a definite enhancement in the rate of polymerisation when the halide is changed from chlorine to fluorine. As the first step in the polymerisation is the formation of the diamide this would be expected as it is well known[110] that the nucleophilic substitution of fluorides proceeds much faster than the corresponding chlorides.

An interesting aspect of this work was the formation of cross linked and gelled polymer when 4,4' difluorodiphenyl sulphone was used as the cocatalyst. The gelled and insoluble material was formed at the higher catalyst concentrations. No cross-linked polymer was observed when p fluoro phenyl sulphone was used as the cocatalyst. The ease with which the cross-linking reactions take place in the case of the difluoro derivatives is undoubtedly related to the enhanced rate of nucleophilic substitution of these compounds. A reaction was proposed to explain these observations.[71]

4,4' diamino diphenyl sulphone and diphenyl sulphone do not act as cocatalysts in the polymerisation of caprolactam. In the former the overall electron donating effect of the amino group reflects the ease with which the nitrogen atom releases its lone pair electrons which is more than sufficient to outweigh the inductive effect of the group. The amino groups are therefore not susceptible to nucleophilic substitution. Whether or not diphenyl sulphone will initiate polymerisation depends on the effect of the sulphonyl group on the π electron density in the phenyl group, and in particular on the carbon atoms in the 4 and 4' positions. The sulphonyl group is an electron withdrawing group with a large part of its electron attracting power being due to its inductive effect. The carbon atoms in the 4 and 4' positions will have a reduced electron density but the effect is not strong enough to cause diphenyl sulphone to initiate polymerisation.

Diphenyl ether does not act as a cocatalyst in the anionic polymerisation of caprolactam because the lactam anions are not basic enough to cause cleavage of the ether linkage, even at 150°C.

When sodium hydride is added to caprolactam containing diphenyl ether it reacts with is in preference to the monomer, by the reaction shown below (equation 25).



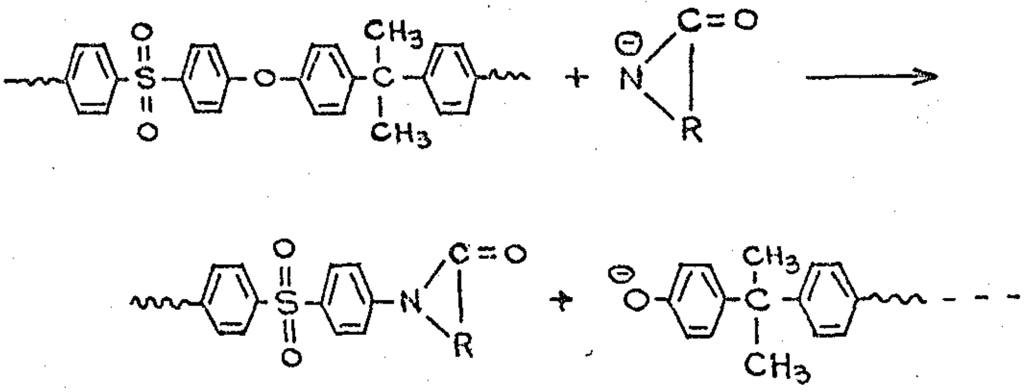
(25)

red coloured

The colour of the solution changes from colourless to red, the intensity depending on the concentrations of sodium hydride and diphenyl ether. Although the sodium hydride, which is a strong base, is capable of cleaving the ether linkage no polymerisation occure because the species formed is not basic enough to react with caprolactam to form lactam anions.

3:22.7 PROPOSED REACTION MECHANISM.

By taking into consideration the results of the experiments to determine the copolymer composition, the molecular weight of thepolysulphone components of the copolymers and the attempted polymerisation with alternative cocatalysts it is possible to propose a reaction mechanism which explains all the observations. The reaction mechanism for the anionic polymerisation of caprolactam using polysulphone as the cocatalyst is shown schematically below (equation 26)



(26)

F G

The first step in the polymerisation is the formation of lactam anions by the reaction of sodium hydride with the monomer (equation 21). The ether linkage is then cleaved by the lactam anion because the effect of the electron withdrawing sulphonyl group and the lone pair of electrons on the oxygen make it liable to attack.

It is readily seen that species F is equivalent to the one which is obtained with 4,4' dichlorodiphenyl sulphone. Once formed it reacts rapidly with a lactam anion and polymerisation proceeds by the usual mechanism to give high molecular weight polymer.

This mechanism would be expected to give block copolymers in which a long polycaprolactam chain is attached to part of a polysulphone molecule, the length of the polysulphone component being dependent on the position of the cleavage. Because of the number of reaction sites in a polysulphone molecule it is expected that any one polysulphone molecule will be cleaved more than once and that both AB and ABA type block copolymers will be formed.

A reaction mechanism involving a chain scission reaction explains why it is possible to extract uncombined polysulphone and why there is never 100% incorporation, whatever the catalyst concentration. It also explains why the molecular weights of the polysulphone components of the copolymers are small.

Additional evidence supporting this reaction mechanism is obtained from other properties of the copolymers studies and from the optical microscopy studies.

3:23 OTHER PROPERTIES OF THE COPOLYMERS.

3:23.1 SOLUTION PROPERTIES.

The solubility of the homopolymers and copolymers in pure and mixed solvents at room temperature was studied. The results are shown in Table 17.

TABLE 17.

SOLUTION PROPERTIES.

SOLVENT.	SOLUBLE POLYMERS	INSOLUBLE POLYMERS
FORMIC ACID	NYLON 6	POLYSULPHONE THE COPOLYMERS[a]
M CRESOL	NYLON 6	POLYSULPHONE THE COPOLYMERS[b]
CHLOROFORM	POLYSULPHONE	NYLON 6 THE COPOLYMERS
TOLUENE	POLYSULPHONE	NYLON 6 THE COPOLYMERS
FORMIC ACID/ CHLOROFORM 1:1	NYLON6 POLYSULPHONE THE COPOLYMERS	NONE[c]
FORMIC ACID/ TOLUENE 1:1	NYLON 6 POLYSULPHONE THE COPOLYMERS	NONE[c]

a. The polycaprolactam components of the copolymers are very swollen by the formic acid.

b. The copolymers are very slightly soluble in m cresol but are insoluble at the concentrations chosen.

c. The homopolymers are soluble in the mixed solvents at the concentrations chosen but are not as soluble in them as they are in the respective pure solvents.

All the polymer solubility experiments were made on polymers which had been extracted with water and chloroform to remove any monomer and uncombined polysulphone respectively.

In formic acid the copolymers became very swollen but did not dissolve. Increasing the volume of solvent caused further swelling but not solution. As nylon 6 homopolymer is readily soluble in formic acid the results provide additional evidence that a copolymer is formed during the polymerisation of caprolactam in the presence of dissolved polysulphone. If the polycaprolactam were not in the form of a copolymer it would have dissolved in the formic acid and the polysulphone, being insoluble, would have settled out at the bottom of the tube.

In m-cresol the copolymers are very slightly soluble providing more evidence of copolymer formation. As nylon 6 is readily soluble in m-cresol the polycaprolactam formed should have dissolved if it was present as homopolymer. Polysulphone is insoluble in both formic acid and m-cresol but it appears that m-cresol is capable of dissolving small amounts of low molecular weight polysulphone as the copolymers are soluble in very dilute solutions.

In toluene and chloroform, the two solvents for polysulphone used, the copolymers appear to be completely insoluble. The polysulphone components of the copolymers probably dissolve in the solvents but there is no observable evidence for this.

In the two mixed solvents, one for each component of the copolymers, the copolymers are soluble at the concentrations employed. Although they are soluble in both solvents the copolymers dissolve more readily in the formic acid/chloroform mixture because chloroform is a better solvent for polysulphone than toluene. Although nylon 6 and polysulphone homopolymers are soluble in the mixed solvents at the concentrations employed they are not nearly as soluble as they are in their respective pure solvents.

3.23.2 COPOLYMER DENSITY.

The copolymer densities were measured using samples cut from unused impact specimens which were free from flaws. A straight line graph was obtained when a plot of cathetometer readings versus float density was plotted so that the polymer densities could be calculated from it. The density of the polysulphone homopolymers used to prepare the copolymers was also measured. Each result shown in Table 18 is the average value from at least four samples.

The results show that the densities of the copolymers are similar which is what would have been predicted from the work to determine the copolymer composition and reaction mechanism. The molecular weight determinations show that during the polymerisation the polysulphone molecule is cleaved by a chain scission reaction so that the amount of polysulphone incorporated into each polymer molecule is small.

TABLE 18.

POLYMER DENSITIES.

POLYMER.	% POLYSULPHONE IN POLYMER.	DENSITY (Kg/1)
E6	4.97	1.142
H2	4.99	1.149
F8	10.02	1.144
J12	9.98	1.152
G10	15.00	1.145
K9	9.99	1.151
P1700	100.0	1.237
P3500	100.0	1.240.

This indicates that the densities of the copolymers should be little different from that of nylon 6 and this is what was found. The literature value for the density of nylon 6 is usually quoted as 1.14 Kg/1 slightly less than that determined for the copolymers. The slightly higher density for the copolymers prepared with the higher catalyst concentrations is probably due to better packing of the molecules because of their lower molecular weight and crystallite size.

3.23.3 THERMAL ANALYSIS.

The crystalline melting point of a sample of nylon 6 homopolymer prepared by anionic polymerisation, and the melting points of the polycaprolactam components of the copolymers were measured and the results are shown in Table 19. Figure 11 shows the traces obtained for the copolymers, all of which were similar, and for the nybn 6 homopolymer.

TYPICAL D.S.C. TRACES FOR THE COPOLYMERS AND A NYLON 6 HOMOPOLYMER

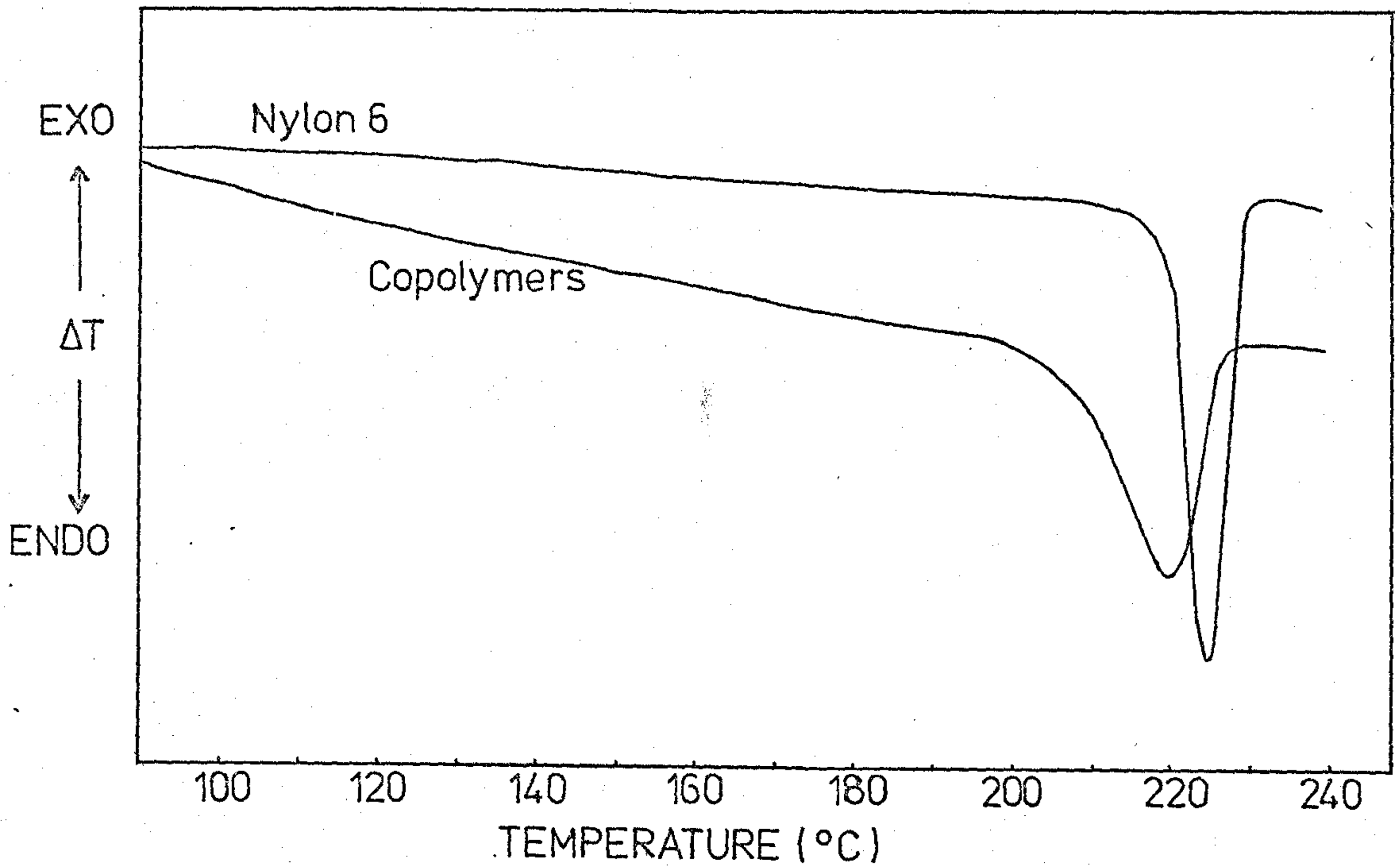


FIGURE 11

TABLE 19.

CRYSTALLINE MELTING POINTS OF NYLON 6 THE POLYCAPROLACTAM POLYSULPHONE COPOLYMERS.

POLYMER	% POLYSULPHONE IN POLYMER	CRYSTALLINE MELTING POINT (°C)
NYLON 6	0	225
E8	5.02	222
H12	4.99	220
F10	10.00	223
J9	9.99	220
G9	15.00	221
K1	9.99	220

Although Figure 11 illustrates only part of the melting curve of the nylon 6 homopolymer and all the copolymers they were subjected to thermal analysis between -100 and 280°C.

The most important information obtained from these curves is the crystalline melting points of the polycaprolactam components of the copolymers and the nylon 6 homopolymer. The melting points quoted in Table 19 are taken as the lowest point on the melting endotherm. The shape of the melting curves for the copolymers indicates the presence of a second component. The nylon 6 homopolymer has a sharp melting endotherm while the polycaprolactam components of the copolymers have broad melting endotherms. The temperature range of the melting endotherms of the copolymers was 14-18 degrees C compared with 6 degrees for the homopolymer. The melting points of the copolymers are slightly lower than those of the homopolymer. Taking into consideration the sample weights, the areas enclosed by the melting endotherms indicates that the degree of crystallinity of the copolymers is slightly less than that of the nylon 6.

It is not unexpected that copolymer formation will reduce the degree of crystallinity by a small amount. This reduction could account for the small differences in density between the copolymers prepared with the different catalyst concentrations. Increasing the catalyst concentration should increase the amount of amorphous polymer which will arrange itself better and give polymers with higher densities. There should also be a slight reduction in the crystalline melting point of the polycaprolactam component of the copolymers and this is what is observed.

There is no evidence of monomer in the copolymers.

It is known that crystalline polymers are in fact only partially crystalline.. The two phase structure of a partially crystalline polymer is considered to consist of geometrically perfect regions, crystallites, surrounded by amorphous regions. The maximum crystallinity that can be obtained varies with the nature of the repeating unit. High crystallinity, 40-50% is obtained with polymers such as nylons because their regular structures permit chain alignment and a high degree of hydrogen bonding.

The lower melting temperature and broader melting range of low density polyethylene compared with that of high density polyethylene is a direct result of the wide distribution of crystallite sizes. Also, the gradual melting point depression of copolymers containing a small percentage of a second component is interpreted as being due to interference with the crystalline structure by this component.

It would therefore seem probable that the broader melting curve for the copolymers is due to a combination of these effects.

Photographs of sections of the copolymers and nylon 6 homopolymers (page 134) shows the latter to have more regular spherulites. Because there is only a small difference in the molecular weight of the segments of polysulphone attached to the polycaprolactam it would be expected that there would only be a small decrease in the crystalline melting point and this is what was found.

3:23.4 APPEARANCE OF THE COPOLYMERS.

The colour and appearance of the copolymers prepared with various catalyst concentrations, polysulphone concentrations and polymerisation times were noted. The change in colour of shavings of the copolymers when they were exposed to air and moisture was also noted. Moulded copolymers appeared to have better thermal stability than the polycaprolactam homopolymers.

Copolymers prepared with catalyst concentrations of less than 0.75 mole % were almost colourless, or a very pale pink colour. When the catalyst concentration was increased to 1 mole % the copolymers had a definite pink colour but there also seemed to be a thin white sheath around the polymer. At catalyst concentrations of about 2 mole % the copolymers had a yellow-orange colour which became more orange as the catalyst concentration was increased. The copolymer prepared with a catalyst concentration of 5 mole % was an intense orange colour. Shavings of most of the copolymers were found to give a white polymer after standing in the atmosphere for a period of time.

Copolymers prepared with catalyst concentrations of 1 mole % were usually white after standing overnight, those prepared with a catalyst concentration of 2 mole % took a little longer. The copolymer prepared using a very high catalyst concentration did not give a really white colour, even after extraction with water.

The most probably cause of the colour in the copolymers is ions which were not able to terminate when the polycaprolactam crystallised. The higher the catalyst concentration the greater the number of ions formed and more intense is the colour of the polymer. When exposed to air and moisture these ions react readily with a resulting loss of colour.

The better heat resistance of the copolymers compared with the nylon 6 homopolymer is undoubtedly due to the polysulphone which has good heat resistant properties. These properties appear to be retained by the polymer even though it undergoes chain scission reactions during the polymerisation.

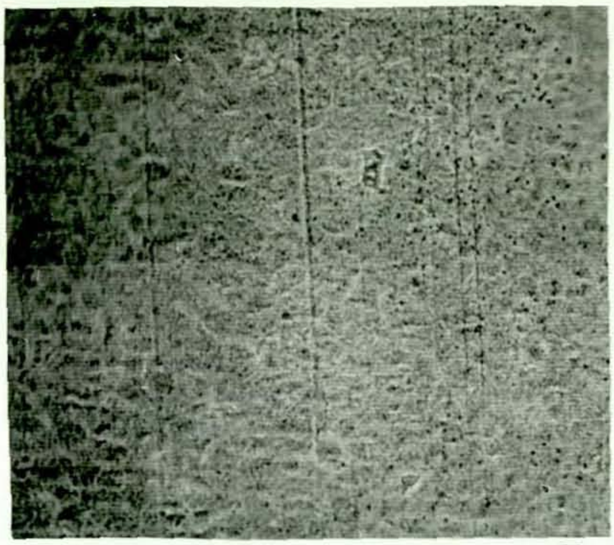
3:24 OPTICAL MICROSCOPY.

Sections of the copolymers and a nylon 6 homopolymer were prepared as described (page 92) and the results are shown in plates 1 - 9. Conditions appropriate to the plates are given in Table 20.

TABLE 20.

PLATE NUMBER	POLYSULPHONE CONTENT (%)	MAGNIFICATION X	MODE
1	5	64	PHASE CONTRAST.
2	10	64	"
3	15	64	"
4	10	160	CROSS POLARS
5	15	160	"
6	0	160	"
7	10	160	PHASE CONTRAST.
8	15	160	"
9	0	160	"

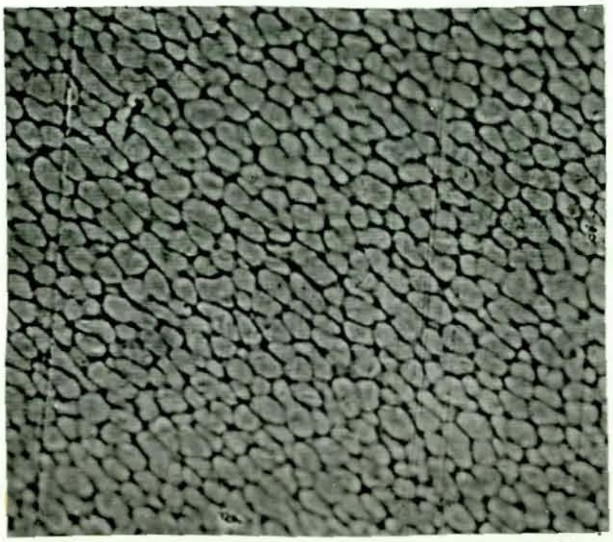
Plates 1-3 are phase contrast photomicrographs of polycaprolactam-polysulphone copolymers containing 5,10 and 15% by weight of polysulphone respectively. Plate 1 shows that the copolymers containing 5% by weight have a continuous phase of polycaprolactam and a dispersed phase of polysulphone. The plate shows the dispersed phase particle size to be very small, which is what would be expected if the polysulphone molecule is broken during polymerisation. The small size of the dispersed phase particles explains why any uncombined polysulphone cannot be removed by simple chloroform extraction. It is impossible for the chloroform, which is a non solvent for polycaprolactam, to penetrate the continuous phase.



Copolymer
Containing
5% Polysulphone

Plate 1

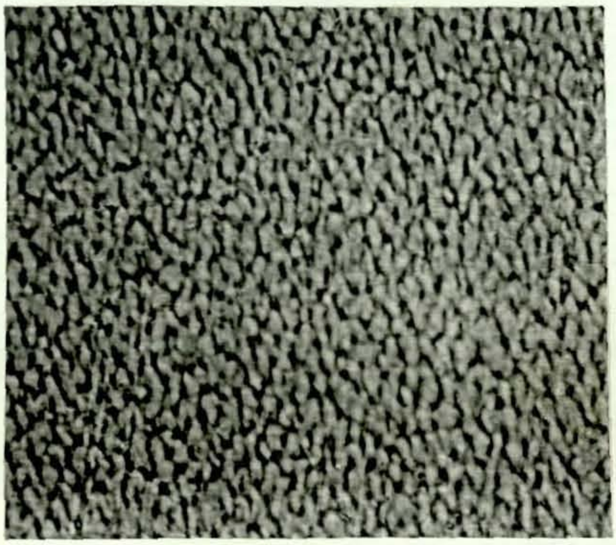
5μ



Copolymer
Containing
10% Polysulphone

Plate 2

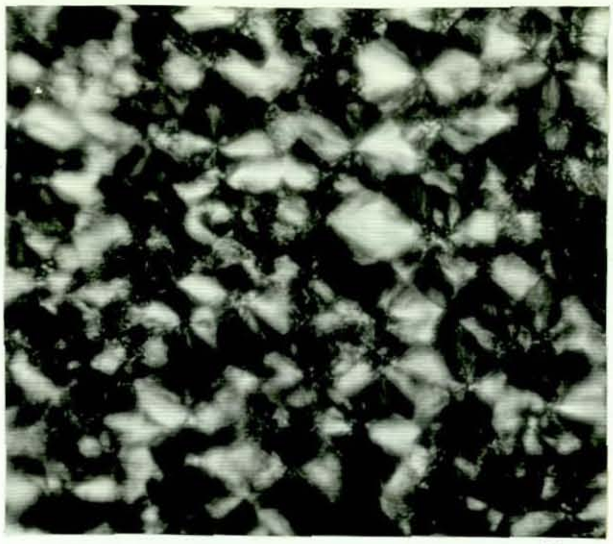
5μ



Copolymer
Containing
15% Polysulphone

Plate 3

5μ



Copolymer
Containing
10% Polysulphone

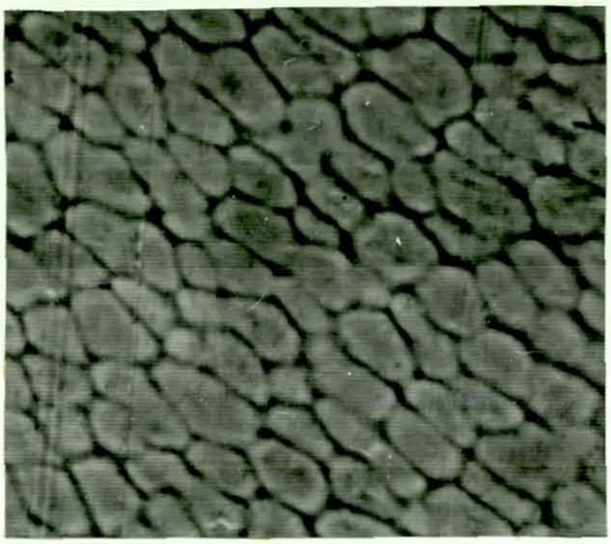
Plate 4

Copolymer
Containing
15% Polysulphone

Plate 5

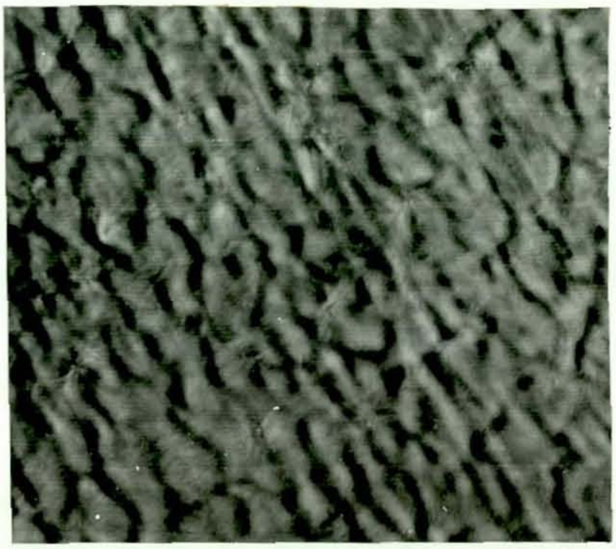
Nylon 6
Homopolymer

Plate 6



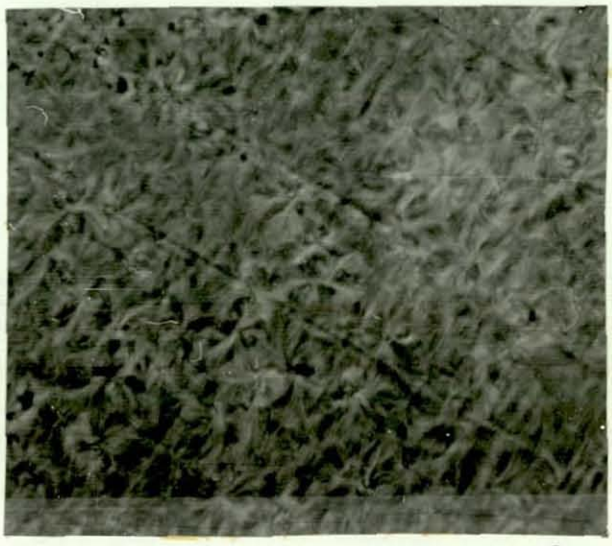
Copolymer
Containing
10% Polysulphone

Plate 7 2μ



Copolymer
Containing
15% Polysulphone

Plate 8 2μ



Nylon 6
Homopolymer

Plate 9 2μ

As the amount of polysulphone in the polymers is increased from 5 to 10% by weight there is a definite change in the phase structure. When the polysulphone concentration is 10% by weight it appears to form a definite continuous phase with the polycaprolactam forming the dispersed phase. However, by using a staining technique it has been shown that the "continuous" phase does in fact contain polycaprolactam. The polycaprolactam will penetrate the "continuous" phase because the molecules are attached to the polysulphone. The "continuous" phase also contains any fragments of polysulphone molecules which are not attached to polycaprolactam. Because the "continuous" phase is a polysulphone rich phase it is possible to extract any uncombined polysulphone by soxhlet extraction with chloroform.

When the polysulphone content is increased to 15% there is a further, but less dramatic change in the phase structure. The phase structure of the copolymers appears to be changing from one with definite continuous and dispersed phases to one where the two phases are interpenetrating. Staining again showed that the polysulphone phase contained polycaprolactam. Because of the phase structure of the polymer it was again possible to extract the uncombined polysulphone by simple soxhlet extraction with chloroform.

Plates 4-6 were taken with the samples viewed through cross polarisers and show the spherulitic structure of the copolymers and a typical nylon 6 homopolymer. Plates 4 and 5 are of polymers containing 10 and 15% by weight of polysulphone respectively and plate 6 is of nylon 6 prepared by direct casting. [redacted]

The ordering could be due to the restraining effect of the polysulphone which has been forced into the continuous phase even though there is no evidence of a two phase structure from these plates.
As the polycaprolactam in the copolymers penetrates the continuous phase it is not unexpected that evidence for the presence of polysulphone is only obtained from the plates taken under phase contrast conditions. Plate 5 shows that, because the molecular weight of the polysulphone in the "continuous" phase is very low, it cannot be seen under cross polars even when the concentration is 15% by weight.

Plates 7-9 are the same sections as plates 4-6 but were taken using a phase contrast condenser. Because of the higher magnification plates 7 and 8 show the phase structure of the polymers containing 10 and 15% of polysulphone in more detail. Plate 9 is of nylon 6 and is used for comparison purposes only.

3:25 PHYSICAL PROPERTIES.

Some physical properties of the copolymers were determined and compared with those of a commercial nylon 6. The copolymers were prepared to the specifications given in Table 13. Tables 1-6 Appendix II give details of all the copolymers prepared and the test to which each was subjected.

3:25.1 TENSILE STRESS-STRAIN TEST.

From each compression moulded sheet twenty dumbell test pieces could be cut. Half were stored in a vacuum descicator over phosphorus pentoxide for at least a week before testing and were known as the "dry" samples.

The remainder were allowed to come to equilibrium in a constant temperature room (23° ± 0.5°C; 65% RH) and were known as the "equilibrated" samples.

Figure 12 shows a typical tensile stress strain curve for a hard, tough polymer.

YIELD POINT

The yield point is the first stress level on the stress-strain curve at which the slope of the curve becomes zero. The term is an arbitary one, in general, since deviations from Hookian behaviour take place before and after the point.

YIELD STRENGTH.

The yield strength of a material is the apparent stress at the yield point, as defined above. At this point a specimen is considered to be damaged, though the damaging effects are considered to be negligible at stresses slightly below the value. The apparent stress, calculated by dividing the load by the original minimum cross sectional area of the test piece, is itself slightly lower than the true stress. The results are expressed in mega Newtons per square metre.

PERCENTAGE ELONGATION AT BREAK.

The percentage elongation at break is the percentage elongation at the moment of rupture. It is calculated by dividing the extension at the moment of rupture of the specimen by the original distance between the gauge marks and multiplying by 100. As such the values are slightly lower than true strains at the moment of rupture.

A TYPICAL TENSILE STRESS-STRAIN CURVE FOR A HARD, TOUGH, POLYMER

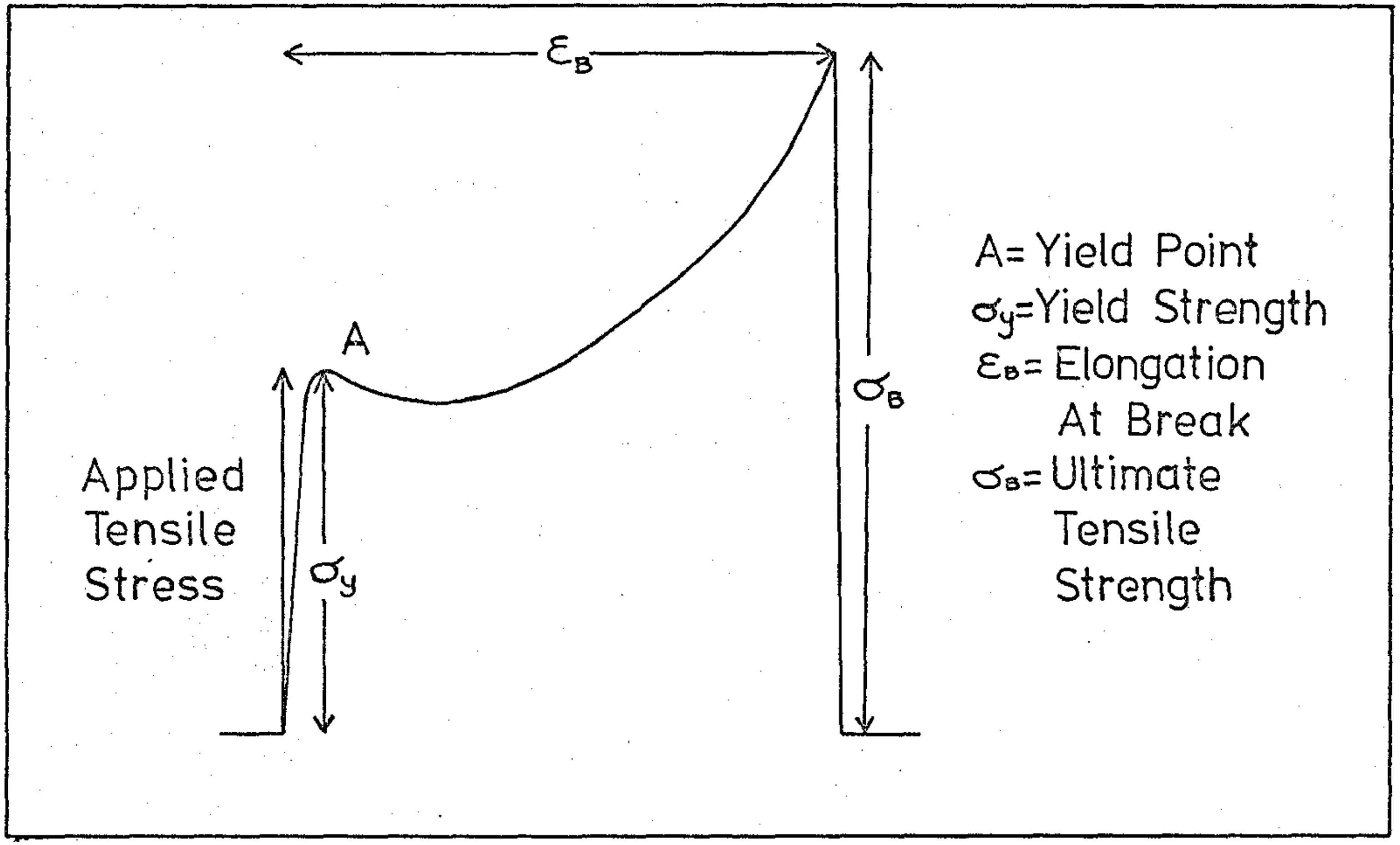


FIGURE 12

ULTIMATE TENSILE STRENGTH.

The true ultimate tensile stress of a material is the tensile stress required to break it, calculated by dividing the load by the cross sectional area of the test specimens at the moment and point of rupture.

In this work the apparent tensile strength at break was determined. The tensile load was divided by the original cross sectional area of the specimen, the results being expressed in mega Newtons per square metre.

RESULTS AND DISCUSSION.

The yield strengths, apparent tensile strengths at break and elongation at break for "equilibrated" samples of the copolymers and nylon 6 homopolymer are given in Table 21.

The yield strengths of all the copolymers were lower than the yield strength of the commercial nylon 6. The yield strengths of the copolymers prepared with catalyst concentrations of 1 mole % were similar, as were those for the copolymers prepared with catalyst concentrations of 2 mole %. The copolymers prepared with the higher catalyst concentration had slightly higher yield strengths than those prepared with the lower catalyst concentration. The yield strength of the copolymers prepared with the higher molecular weight polysulphone was similar to that of other copolymers prepared with a catalyst concentration of 1 mole %.

The tensile strengths at break for all the copolymers were greater than that of the nylon 6 homopolymer.

The copolymers prepared with the lower catalyst concentration had the highest tensile strength at break. As the amount of polysulphone in the copolymers was increased there appeared to be a slight decrease in the tensile strength at break. The copolymers prepared with the higher catalyst concentration appeared to have similar tensile strengths at break. Increasing the molecular weight of the polysulphone used to prepare the copolymers resulted in an increase in the tensile strength at break.

As expected, the elongationsat break for the copolymers and nylon 6 homopolymer followed a similar pattern to the tensile strength at break results.

The tensile properties of the nylon 6 homopolymer and the copolymers were also measured for samples which had been stored in a vacuum descicator. The results are shown in Table 22. For these polymers it was only possible to measure the yield strength and elongation at break. For the copolymers prepared with a catalyst concentration of 1 mole % there appeared to be a small but gradual increase in the yield strength as the polysulphone concentration was increased. The yield strengths of the copolymers prepared with the higher catalyst concentration appeared to be similar. The yield strength of the copolymers appeared to increase as the molecular weight of the polysulphone used to prepare them was increased. The nylon 6 homopolymer had a yield strength similar to that of the copolymer prepared with a catalyst concentration of 1 mole % and a polysulphone concentration of 10% by weight.

TABLE 21.

POLYSULPHONE- POLYCAPROLACTAM COPOLYMERS.

TENSILE PROPERTIES OF "EQUILIBRATED"SAMPLES.

N°.	CATALYST CONCENTRATION (MOLE%)	POLYSULPHONE CONTENT (%)	YIELD STRENGTH (MN/Sq m)	TENSILE STRENGTH AT BREAK. (MN/Sq m)	ELONGATION AT BREAK (%)
E3	1.04	5.02	30.64	73.92	305
E4	1.00	5.01	31.43	72.51	306
E5	0.96	5.01	30.41	68.71	285
E9	1.02	5.00	30.21	76.88	318
F1	1.01	10.01	30.70	65.80	286
F2	0.96	9.95	32.68	68.57	297
F11	0.99	10.02	33.49	66.67	280
F12	0.97	10.02	33.36	74.98	320
G3	0.97	15.00	31.98	67.66	291
G4	1.01	14.96	32.33	62.66	275
G5	0.98	15.02	30.41	66.73	294
G8	1.00	15.08	31.85	66.64	286
H3	2.00	5.00	33.63	56.82	253
H4	1.97	4.97	35.12	67.67	295
H6	1.95	4.97	34.83	66.30	312
H10	2.00	4.98	35.22	57.71	261
J1	1.98	9.98	34.89	64.07	293
J5	2.05	10.04	32.96	65.57	292
J6	1.96	9.97	34.57	63.24	281
J10	2.02	10.00	38.55	55.39	286
K3	1.02	10.04	31.63	71.41	310
K4	1.02	10.00	31.20	73.53	318
K5	0.97	10.01	30.28	68.26	298
K8	1.00	10.01	31.76	73.19	310
N6/1	-	-	44.69	54.92	204
N6/2	-	-	43.84	67.28	306

TABLE 22.

POLYSULPHONE-POLYCAPROLACTAM COPOLYMERS

TENSILE PROPERTIES OF " DRY " SAMPLES.

N^o.	CATALYST CONCENTRATION (MOLE %)	POLYSULPHONE CONTENT (%)	YIELD STRENGTH (MN/sq.m)	ELONGATION AT BREAK. (%)
E3	1.04	5.02	76.76	189
E4	1.00	5.01	75.86	227
E5	0.96	5.01	75.62	240
E9	1.02	5.00	75.51	143
F1	1.01	10.01	81.49	98
F2	0.96	9.95	83.71	170
F11	0.99	10.02	82.68	160
F12	0.97	10.02	81.11	186
G3	2.00	15.00	84.05	167
G4	1.97	14.96	83.55	103
G5	1.95	15.02	83.04	179
G8	2.00	15.08	85.66	124
H3	2.00	5.00	79.02	122
H4	1.97	4.97	77.94	109
H6	1.95	4.98	78.22	76
H10	2.00	4.98	77.42	80
J1	1.98	9.98	78.74	119
J5	2.05	10.04	88.87	74
J6	1.96	9.97	78.34	139
J10	2.02	10.00	84.47	28
K3.	1.02	10.04	84.55	157
K4	1.02	10.00	82.16	139
K5	0.97	10.01	84.17	125
K8	1.00	10.01	83.85	153
N6/1	-	-	82.15	59
N6/2	-	-	83.04	84

FIGURE 13

TENSILE STRESS-STRAIN CURVE
Polysulphone-Polycaprolactam Copolymers
"Equilibrated" Samples

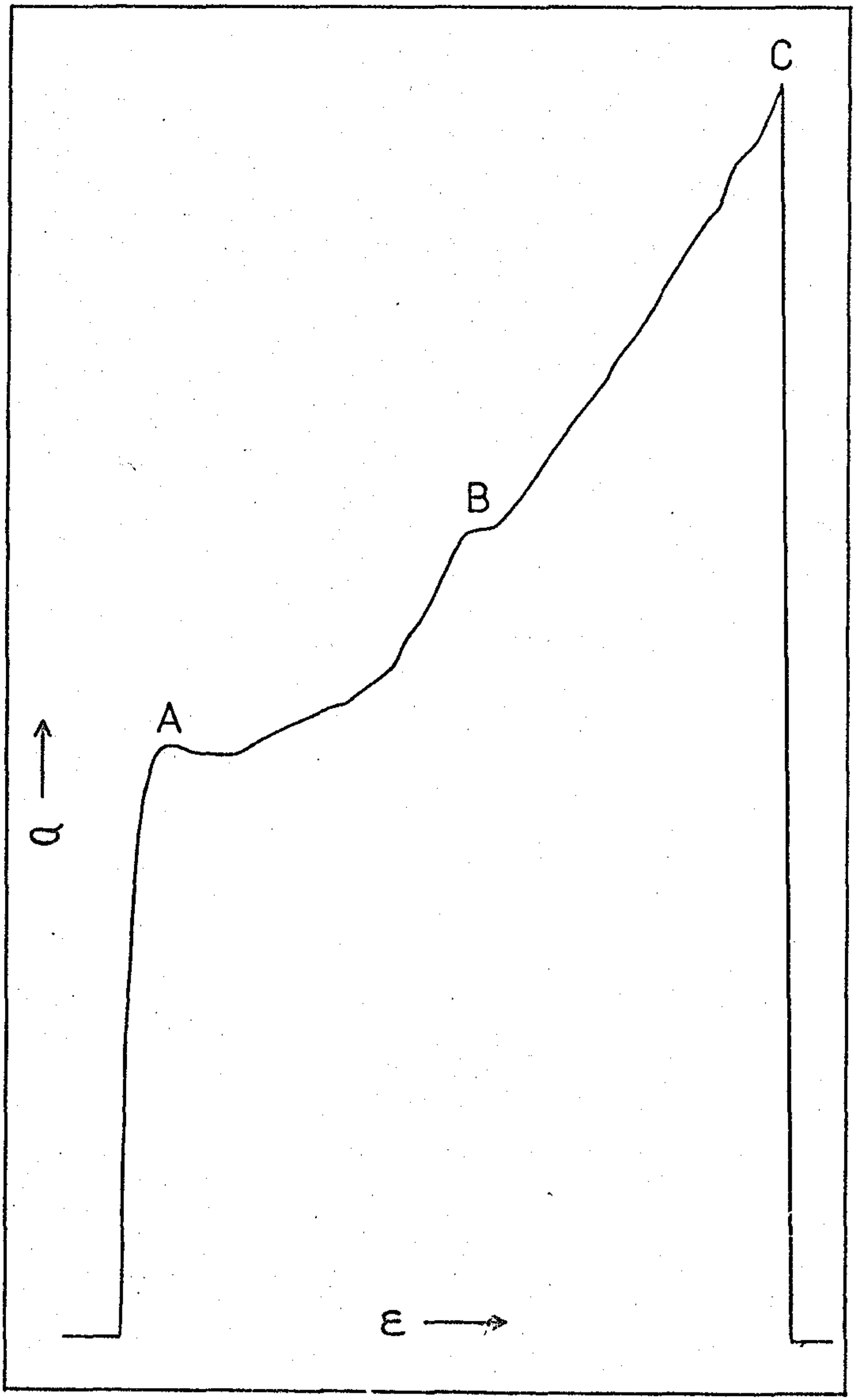


FIGURE 14

TENSILE STRESS-STRAIN CURVE

Nylon 6 Homopolymers

"Equilibrated" Samples

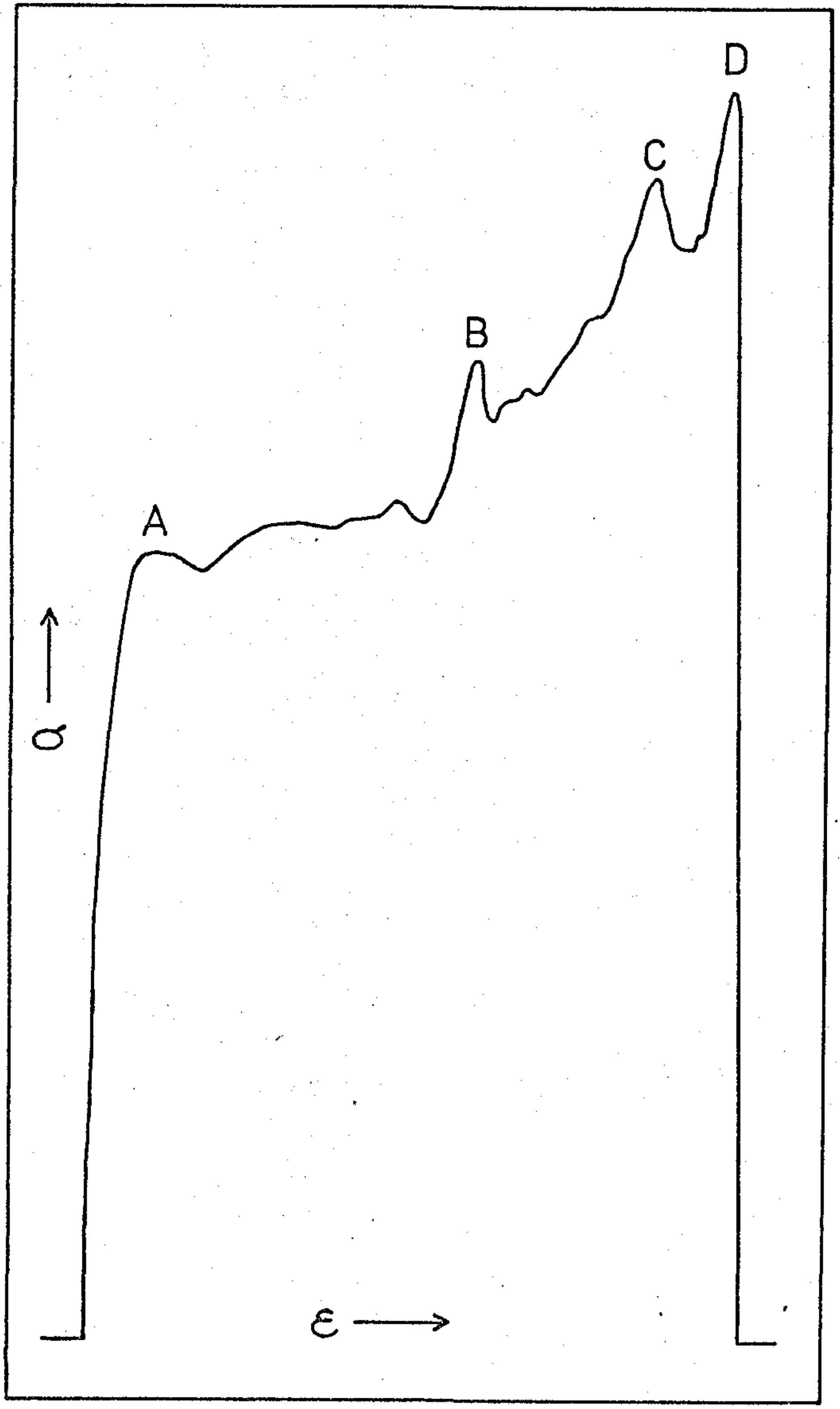
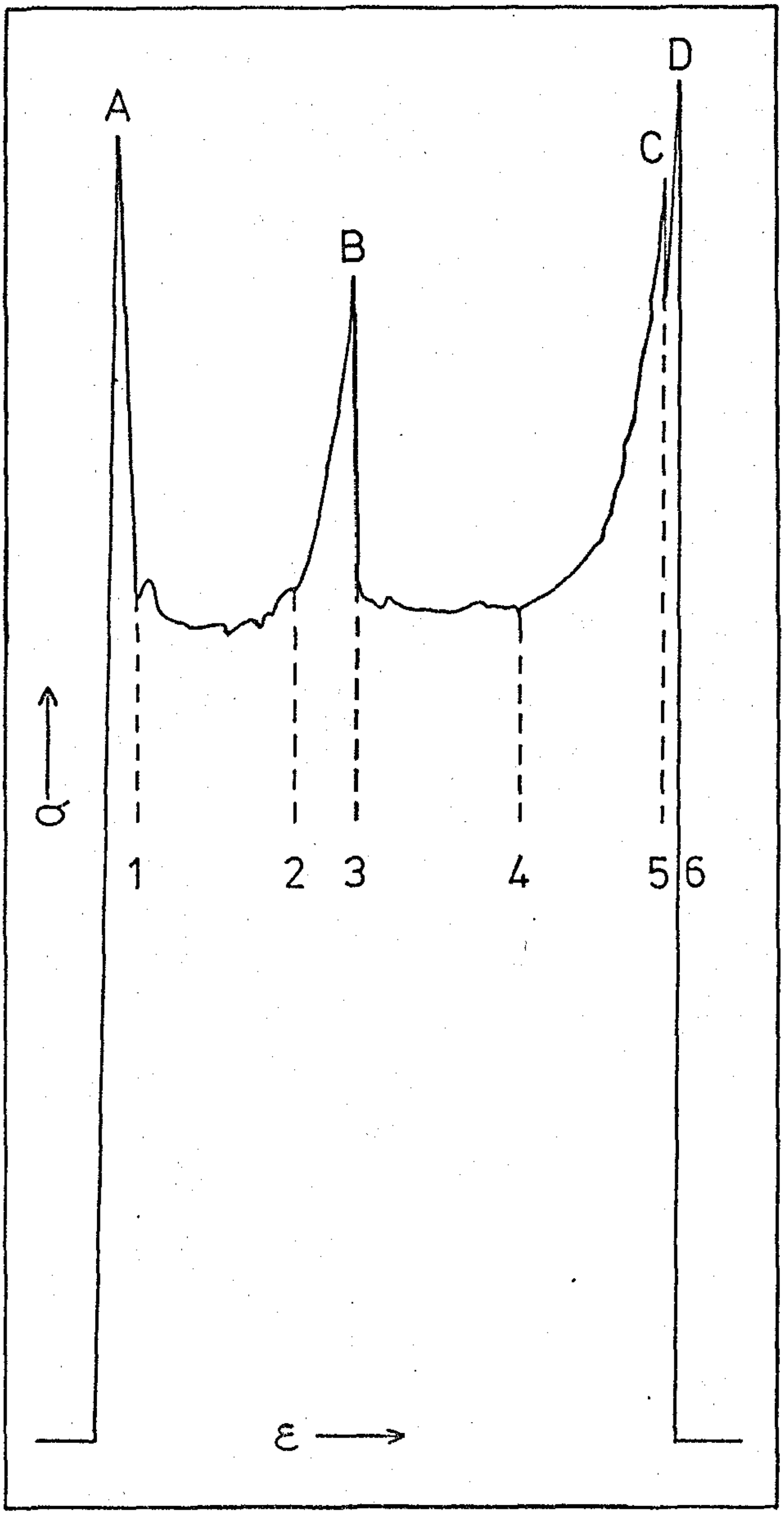


FIGURE 15

TENSILE STRESS-STRAIN CURVE

Copolymers and Nylon 6 Homopolymers

"Dry" Samples.



The elongations at break for the "dry" samples were more scattered than for the "equilibrated" samples. The copolymers prepared with the lower catalyst concentration had the highest elongations at break. The elongation at break decreased as the polysulphone concentration was increased. The copolymers prepared with a catalyst concentration of 2 mole % had similar elongations at break. Increasing the molecular weight of the polysulphone used to prepare the copolymers did not appear to affect the elongation at break. The elongation at break for the nylon 6 homopolymer was less than that of all the copolymers.

Figures 13 and 14 show typical stress-strain curves for "equilibrated" samples of the copolymers and nylon 6 homopolymer respectively. After the samples had been stored in a vacuum descicator the homopolymer and copolymers gave similar stress-strain curves, as illustrated in Figure 15.

When a tensile stress was applied to "equilibrated" samples of the copolymers (Figure 13) they came under tension and then yielded (point A). The samples yielded by necking and then elongated by drawing in a regular manner towards one of the jaws until the width of the dumbell test piece started to increase. At this point there was a slight increase in the stress before the sample "yielded" again (point B) and elongated by drawing towards the opposite jaw. When the whole of the test area had elongated the sample came under tension again and finally broke (point C). None of the samples "yielded" again after the test area had become fully elongated.

Although the overall shape of the stress-strain curve for the "equilibrated" samples of the homopolymer (Figure 14) were similar to those for the copolymers there were several noticeable differences. The yield point (point A) for the homopolymer was more pronounced that those for the copolymers but it did not draw so easily. When the sample had elongated to the point where the width of the test piece started to increase there was a sharp increase in the stress before it yielded again (point B). There was another sharp increase in the stress when the test piece became fully extended and the sample either broke, or "yielded" again (point C) at any point along its elongated length. Samples which "yielded" again only elongated a few more percent before breaking (point D).

Drying the polymers had a marked effect on their tensile properties as illustrated in Figure 15. The tensile stress-strain curves for the copolymers and homopolymer were similar. The yield strengths of the "dry" samples were much greater than those of the "equilibrated" samples but their elongations at break were less, especially for the homopolymer and the copolymers prepared with the higher catalyst concentration. Because of this the "dry" samples were only occasionally fully extended as illustrated in Figure 15.

Samples which became fully extended when a tensile stress was applied, yielded (point A) and "yielded" twice more (points B and C) before breaking (point D). Most of the samples broke before becoming fully extended and, as expected, there were several points where this occurred. It turned out that the points at which the samples broke (1-6) appeared to fall into two groups.

They either broke as soon as the sample had yielded (1,3 and 5) or at the point where the sample had become fully extended towards one of the jaws and the stress started to increase (2 and 4). When point C was reached, and the sample "yielded" again without breaking, it only elongated a few more percent before it did so.

The tensile stress-strain curves for the "equilibrated" samples show that the copolymers are hard, tough materials. The areas under the stress-strain curves indicates that they have greater tensile strengths at break than the homopolymer. The shape of the stress strain curves shows that the copolymers yield and elongate more readily than the commercial nylon 6 and indicates that they could be suitable for fibre forming.

The results given in Table 21 show that, although the copolymers have yield strengths which are lower than that of the commercial nylon 6, their tensile strengths and elongations at break are greater. The tensile strengths at break given are in fact apparent tensile strengths at break because they do not take into account changes in the cross sectional area of the samples as they elongate. Because of this the trends indicated are more pronounced and the tensile properties of the copolymer are improved with respect to those of the homopolymer.

The results indicate that the degree of crystallinity and molecular weight of the polycaprolactam component of the copolymers are the factors which have most influence on the tensile properties of the copolymers. Thermal analysis indicates that the polysulphone causes a slight reduction in the crystallinity of the polycaprolactam component of the copolymers.

It would be expected that the polycaprolactam components of the copolymers prepared with the lower catalyst concentration would have the highest molecular weight. The results show that these copolymers have better tensile properties than those prepared with the higher catalyst concentration.

Although the tensile stress-strain curves for the copolymers indicates that they could form fibres with a high tensile strength it cannot be assumed that the copolymers with the best tensile properties will form the best fibres. This can only be assessed by actually spinning fibres and all the factors which could affect the fibre forming properties of a polymer must be taken into consideration before any conclusions are drawn.

The "dry" samples were tested in order to determine the effect of the polysulphone on the tensile properties of the copolymers in the absence of water which acts as a plasticiser for the nylon. Sebenda and coworkers[111] have studied the effects of water and unreacted monomer on the physical properties of nylon 6 and showed them to be considerable.

The results show that the molecular weight of the polysulphone components of the copolymers is too low to have any significant effect on their tensile properties. The copolymers in which the molecular weight of the polycaprolactam components is highest are most affected by drying with respect to the yield strength. These long polycaprolactam chains still elongate more readily than shorter ones when subjected to a tensile stress and as a result have higher elongations at break.

3:25.2 IMPACT STRENGTH.

Impact strengths were measured on a Hounsfield Impact testing machine which measures the work done in breaking a notched test piece. The machine measures the Charpy Impact strength of a material and the results are quoted in MKS units, K Joules/m^2 behind the notch.

From the compression moulded "slabs" it was possible to cut twelve test pieces. All the test pieces cut from one "slab" were either allowed to equilibrate in a constant temperature room (23 ± 0.5°C 65% RH) or stored in a vacuum descicator for at least a week before testing. The samples were referred to as the "equilibrated" and "dry" samples respectively and the results are shown in Tables 23 and 24, together with those for a commercial nylon 6.

For the "equilibrated" samples all the copolymers prepared with a catalyst concentration of 1 mole % had better impact strengths than the commercial nylon 6. An increase in the amount of polysulphone in the copolymers resulted in a decrease in the impact strength. The copolymers prepared with catalyst concentrations of 2 mole % had impact strengths which were less than those of the nylon 6 homopolymer. Increasing the molecular weight of the polysulphone used to prepare the copolymers resulted in a decrease in the impact strength.

TABLE 23.

POLYCAPROLACTAM-POLYSULPHONE COPOLYMERS.

IMPACT STRENGTHS : "EQUILIBRATED" SAMPLES.

N°.	CATALYST CONCENTRATION (MOLE%)	POLYSULPHONE CONTENT (%)	CHARPY IMPACT STRENGTH (K JOULES/m^2 BEHIND NOTCH)
E2	0.98	5.02	16.56
E6	0.95	4.97	16.48
E7	0.98	4.98	16.31
E11	0.98	5.00	15.38
F3	1.04	10.00	15.85
F4	1.01	10.02	15.45
F5	0.99	10.01	15.56
G10	0.99	15.00	13.12
G11	0.99	15.03	13.71
G12	0.99	15.02	13.33
H2	1.98	4.99	10.04
H5	1.98	5.00	10.83
H11	1.99	4.98	10.41
H13	1.98	4.99	10.51
J2	2.03	10.01	7.44
J3	1.99	9.99	8.15
J4	2.01	10.00	7.56
K6	1.02	10.01	13.22
K7	0.98	10.03	12.79
K11	1.00	10.02	12.81
N6/5	- 0·98	-	12.11
N6/6	- 0·98	-	12.08

TABLE 24.

POLYCAPROLACTAM-POLYSULPHONE COPOLYMERS.
IMPACT STRENGTHS : "DRY" SAMPLES.

N°.	CATALYST CONCENTRATION (MOLE%)	POLYSULPHONE CONTENT (%)	CHARPY IMPACT STRENGTH (K JOULES/m^2 BEHIND NOTCH)
E10	0.98	4.99	4.36
E12	0.97	5.03	3.96
E13	1.03	5.00	3.20
F6.	1.00	9.97	4.21
F7	1.05	10.00	4.21
F8	0.99	10.02	4.30
F9	1.02	9.99	3.61
G1	1.01	14.99	3.43
G6	0.96	15.02	3.12
G7	1.03	15.01	3.20
H1	2.01	4.99	2.99
H8	1.98	5.00	2.87
H9	1.97	4.99	2.57
J7	2.03	9.99	2.08
J11	2.01	10.00	2.11
J12	2.03	9.98	2.25
K9	1.03	9.98	3.09
K10	1.00	10.04	3.18
K12	1.00	10.02	2.56
N6/3	-	-	5.26
N6/4	-	-	5.31

For the "dry" samples the impact strengths of all the copolymers were lower than that of the commercial nylon 6. The copolymers prepared with the lower catalyst concentration had better impact strengths than those prepared with the higher catalyst concentration. The impact strength decreased as the concentration of polysulphone in the copolymers was increased. Increasing the molecular weight of the polysulphone used to prepare the copolymers resulted in a decrease in their impact strength.

A rough guide to the impact properties of a polymer can often be obtained from calculating the area under its stress-strain curve. As the area under the curve is increased the impact strength or toughness is expected to increase. It might be expected therefore, that the impact strengths of the "equilibrated" samples of the copolymers will be greater than the impact strength of the homopolymer. While this may be the case for many polymers it is important to remember that the tensile test is a slow speed test compared with the impact test and the results need not necessarily be in agreement.

The results indicate that the main factors affecting the impact strengths of the copolymers are the polysulphone concentration and the molecular weight of the polycaprolactam component of the copolymers. Increasing the polysulphone concentration has an adverse effect on the impact properties of the copolymers, increasing the molecular weight of the polycaprolactam component has a favourable effect. The effects act in such a way that the copolymers prepared with the lower catalyst concentration have better impact properties than the homopolymer, those prepared with the high catalyst concentration poorer impact properties.

The small amount of unreacted monomer present in the copolymers does not affect their impact properties. Because of the adverse effect of polysulphone on impact properties the area under the tensile curve is only partially successful in predicting the impact properties of the copolymers.

The "dry" samples were again tested in order to determine the effect of water on the impact properties of the copolymers compared to the homopolymer. Drying has a greater effect on the impact properties of the copolymers but it appears that the adverse effect of the polysulphone is not as great. The homopolymer has better impact properties than the copolymers because of its [redacted] slightly higher degree of crystallinity. The presence of small amounts of additives such as antioxidants may have a small effect on the impact properties of the homopolymer.

The results indicate that copolymers with better tensile and impact properties than a commercial nylon 6 can be prepared.

3:26 MECHANICAL MIXING.

BRABENDER PLASTOGRAPH.

When the blends were compression moulded it was found that the "sheets" contained two phases, indicating that the two polymers had not been thoroughly mixed. The "sheets" contained small "lumps" up to 1mm^2, embedded in them. The "lumps", when cut out with a scalpel, were found to be completely soluble in chloroform. An infra red spectram of a film cast from the chloroform solution showed the soluble material to be polysulphone. The Brabender plastograph traces did, however, indicate that the two polymers were reasonably well mixed. It was noted that the surface appearance of the "sheets" was poor.

Nylon 6 and polysulphone will not mix in a Brabender plastograph at 240°C because their relative melt viscosities are not close enough at the mixing temperatures. Raising the temperature and increasing the mixing time resulted in severe degradation of the nylon. Adding the polysulphone and allowing it to reach the mixing temperature before adding the nylon 6 still gave a two phase system. The poor surface appearance of the moulded "sheets" was undoubtedly due to the incompatibility of the polymers under the mixing conditions. Other attempts at blending polysulphone and polycaprolactam have also been unsuccessful.[112]

4. POLYMER BLENDS WITH POLYCAPROLACTAM.

4:1 EXPERIMENTAL.

4:11 MATERIALS.

CAPROLACTAM
SODIUM HYDRIDE
N-ACETYL CAPROLACTAM

} were purified as described previously (page 52).

POLYMERS.

POLYSTYRENE (LUSTREX HFSS. MONSANTO LTD.)

IMPACT STYRENE (LUSTRES HT 42-1. MONSANTO LTD.)

THERMOPLASTIC RUBBER (TR 3202 SHELL)

These polymers, used in the preparation of the polymer blends, were dried overnight in a vacuum oven at room temperature before use.

NYLON 6 (MARINYL F/106 I.C.I.)

The physical properties of this polymer, a typical nylon 6 homopolymer, were measured and compared with those of the polymer blends and polycaprolactam homopolymers prepared in the laboratory.

4:12 PREPARATION OF POLYMER BLENDS.

The required weights of polymer and caprolactam were weighed into a polymerisation tube and dried overnight in a vacuum oven at room temperature. The polymerisation tube was then fitted with a nitrogen bubbler and placed in a constant temperature bath (150 ± 0.5°C). As in the case of the copolymers, the initial weight of caprolactam took into account losses due to sublimation during the course of the polymerisation. When all the polymer had dissolved the required weight of sodium hydride catalyst was added by the method described previously (page 57).

When all the catalyst had reacted, indicated by the evolution of no more bubbles of hydrogen, the required volume of N-acetyl caprolactam was added from a microsyringe. The nitrogen bubbler was raised above the level of the mixture when the viscosity started to increase markedly. A nitrogen atmosphere was maintained above the polymerising mixture during the course of the polymerisation. At the end of the polymerisation period which was 2 hours, the tube was removed from the constant temperature bath and cooled quickly. The final polymer was weighed as soon as possible after the polymer had cooled.

4:13. CAPROLACTAM HOMOPOLYMERISATION.

After drying overnight in a vacuum oven at room temperature, a polymerisation tube containing the required weight of caprolactam was fitted with a nitrogen bubbler and placed in a constant temperature bath ($150 \pm 0.5^{\circ}C$). The sodium hydride catalyst was added in the usual way, and when it had all reacted the required volume of N-acetyl caprolactam cocatalyst was added from a microsyringe. A nitrogen atmosphere was maintained above the polymerising mixture for the duration of the polymerisation which was 2 hours. The polymer was weighed as soon as possible after the polymerisation tube had been removed from the constant temperature bath.

4:14. MONOMER CONVERSION.

The amount of caprolactam converted to polycaprolactam in the polymer blends and homopolymers was determined by extracting shavings of the polymers in a soxhlet extraction apparatus using water as the solvent. It as found that 24 hours was sufficient to remove all the unreacted monomer and low molecular weight polymer. The shavings were weighed and dried by the method described previously (page 86).

4:15 MOULDING THE POLYMER BLENDS AND POLYCAPROLACTAM HOMOPOLYMERS.

The polymer blends and polycaprolactam homopolymers were moulded in a way similar to that for the polycaprolactam-polysulphone copolymers. The main difference was that all the polymers could be moulded at 230°C, whereas some of the copolymers had to be moulded at higher temperatures. It was found that, as the amount of the second component in the blends was increased the surface appearance of the moulded polymers became rougher and more heterogeneous. The polymer blends and homopolymers flowed to fill the moulds in a way similar to that for the copolymers.

4:16 THERMAL ANALYSIS.

The thermal properties of the polymer blends and polycaprolactam homopolymers were examined on a Du Pont 900 thermal analyser using the technique described for the copolymers (page 91).

4:17 OPTICAL MICROSCOPY.

Sections of the polymer blends were prepared and examined by the techniques used for the copolymers (page 92).

4.18 PHYSICAL PROPERTIES.

The test methods used to determine the tensile stress-strain and impact properties of the polymer blends and polycaprolactam homopolymers were the same as those described for the copolymers (pages 96 and 97).

4:2 RESULTS AND DISCUSSION.

4:21. POLYMER BLEND COMPOSITION.

The effect of catalyst concentration, cocatalyst concentration and time on the polymerisation of caprolactam in the presence of polystyrene was studied. Two series of polymers, each containing 10% by weight of polystyrene, were prepared. For each series the polymerisation time and cocatalyst concentration were kept constant but the catalyst concentration was varied. In the first series the polymerisation time was two hours and the cocatalyst concentration (based on monomer) was 0.17 mole %. In the second series the polymerisation time was four hours and the cocatalyst concentration was 0.28mole %. The amount of monomer converted to polymer was determined by extracting shavings of the blends with water in a soxhlet extraction apparatus for 24 hours. The results are given in Tables 25 and 26 and illustrated in Figure 16.

Before any blends were prepared to determine the effect of a second component on the properties of polycaprolactam two series of polymer blends with polystyrene were prepared in order to determine suitable conditions for their preparation.

Figure 16 shows the conversion of monomer to polymer for the two series. It shows that for catalyst concentrations above 0.4 mole % there is little difference in the conversion of monomer to polymer with cocatalyst concentration and time. Between 0.15 and 0.40 mole % there is a slightly better conversion of monomer for polymers prepared with the higher cocatalyst concentration and polymerisation time of 4 hours.

TABLE 25.

POLYSTYRENE-POLYCAPROLACTAM POLYMER BLENDS.

POLYMERISATION TIME 2 HOURS.

L SERIES No.	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE %)	POLYSTYRENE IN FINAL POLYMER (%)	CONVERSION OF MONOMER TO POLYMER (%)
L1	0.68	0.17	10.21	95.28
L2	0.41	0.17	10.19	95.11
L3	1.53	0.17	10.15	93.76
L4	0.48	0.17	10.09	95.93
L5	1.68	0.17	10.02	95.73
L6	2.53	0.17	10.13	94.56
L7	0.65	0.17	10.08	94.95
L8	1.15	0.17	10.03	95.57
L9	0.93	0.17	10.02	95.21
L10	0.25	0.17	10.03	95.59
L11	0.52	0.17	10.02	94.93
L12	2.00	0.17	10.03	94.21

TABLE 26.

POLYCAPROLACTAM-POLYSTYRENE POLYMER BLENDS.

POLYMERISATION TIME 4 HOURS.

M SERIES No.	CATALYST CONCENTRATION (MOLE%)	COCATALYST CONCENTRATION (MOLE %)	POLYSTYRENE IN FINAL POLYMER (%)	CONVERSION OF MONOMER TO POLYMER (%)
M1	1.73	0.28	10.12	94.97
M2	0.81	0.28	10.03	94.54
M3	0.74	0.28	10.06	95.01
M4	1.64	0.28	10.05	94.69
M5	0.48	0.28	10.09	94.75
M6	1.27	0.28	10.07	94.62
M7	0.33	0.28	10.03	94.47
M8	1.11	0.28	10.13	95.81
M9	1.40	0.28	10.02	95.27
M10	2.63	0.28	10.04	93.74
M11	0.99	0.28	10.03	95.50
M12	0.58	0.28	10.09	95.87
M13	0.21	0.28	10.01	31.21

MONOMER CONVERSION WITH TIME AND CATALYST CONCENTRATION

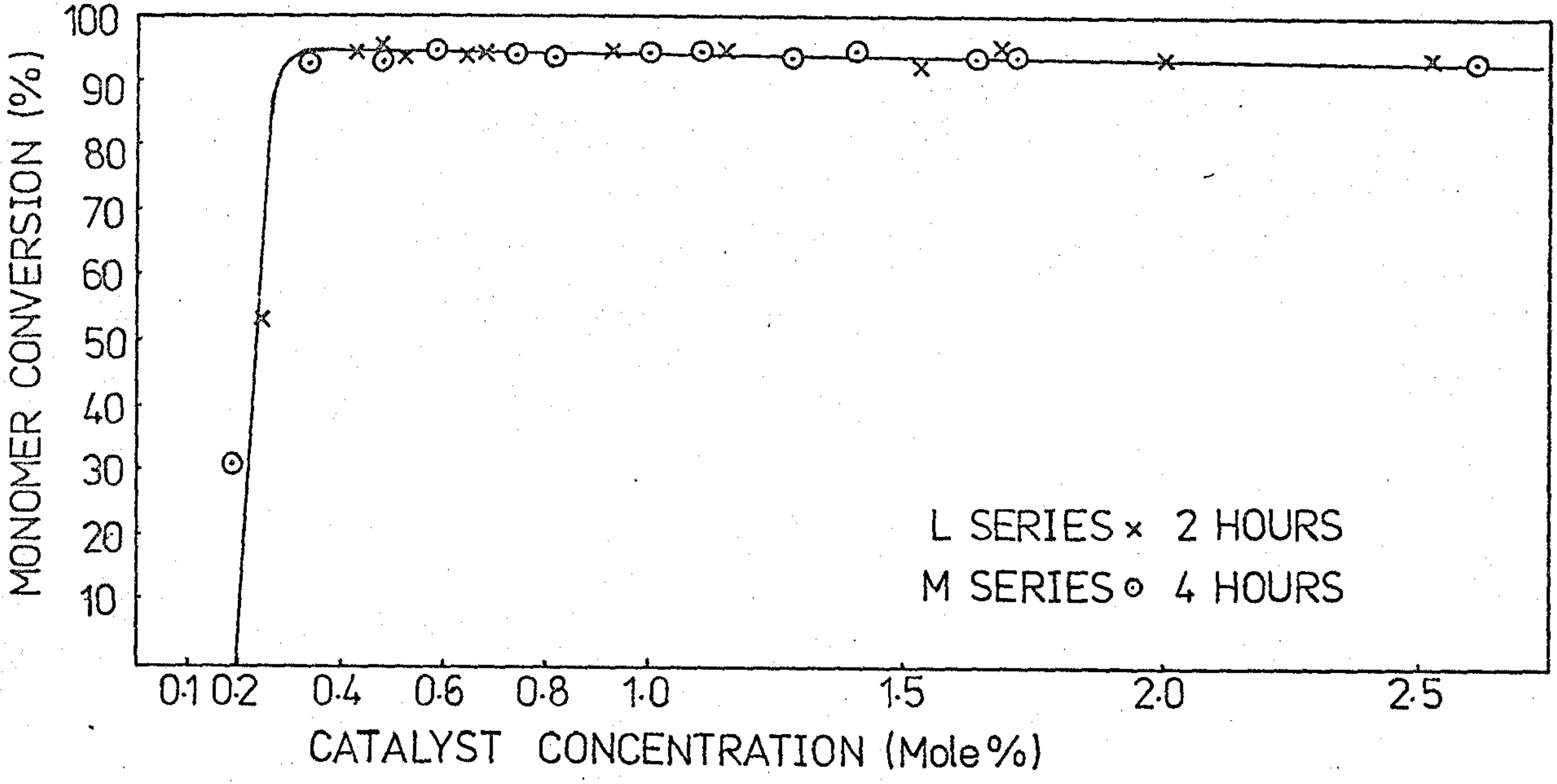


FIGURE 16

At very low catalyst concentrations, below about 0.15 mole % no polymerisation occurs because degradation reactions destroy all the catalyst and lactam anions formed. For catalyst concentrations between 0.15 and 0.60 mole % the conversion of monomer rises rapidly to 90% and then more slowly to a limiting value which is 94.5 ± 1%. As the catalyst concentration is increased from 0.6 to 2.2 mole% the conversion of monomer to polymer remains constant within the values given above. For blends prepared with high catalyst concentrations, above 2.5 mole%, there is a decrease in the conversion of monomer. This decrease can readily be explained in terms of the degradation reactions which occur in lactam polymerisation (APPENDIX I)

From these results it was decided to prepare the polymer blends to the specifications given in Table 27.

4:22. POLYMER BLENDS AND POLYCAPROLACTAM HOMOPOLYMERS.

Polymer blends with polycaprolactam were prepared in order to compare them with a commercial nylon 6 and polycaprolactam homopolymers prepared in the laboratory. Polymer blends were prepared using polycaprolactam as the main component with polystyrene, impact styrene and styrene-butadiene-styrene thermoplastic rubber as the second component. Limits were set on the amount of the second component of the blend and the catalyst and cocatalyst concentrations. For all the polymer blends the polymerisation time was two hours. The blends were prepared to the specifications given in Table 27.

TABLE 27.

SERIES	SECOND COMPONENT IN THE BLEND.	% SECOND COMPONENT IN THE BLEND.	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE %)
S	POLYSTYRENE	5 ± 0.05	1 ± 0.05	0.10 ± 0.02
T		5 ± 0.05	2 ± 0.05	0.21 ± 0.02
U		10 ± 0.05	2 ± 0.05	0.22 ± 0.02
V		15 ± 0.08	2 ± 0.08	0.25 ± 0.03
W	IMPACT STYRENE	5 ± 0.05	1 ± 0.05	0.10 ± 0.02
X		5 ± 0.05	2 ± 0.05	0.21 ± 0.02
Y		10 ± 0.05	2 ± 0.05	0.22 ± 0.02
Z		15 ± 0.08	2 ± 0.08	0.25 ± 0.02
AA	THERMO-PLASTIC RUBBER	5 ± 0.10	2 ± 0.05	0.21 ± 0.02
BB		10 ± 0.10	2 ± 0.05	0.22 ± 0.02
CC		15 ± 0.10	2 ± 0.08	0.25 ± 0.03

Polycaprolactam polymers were prepared to the specifications given in Table 28.

TABLE 28.

SERIES	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE %)
N	1 ± 0.05	0.1 ± 0.02
P	2 ± 0.05	0.1 ± 0.02
Q	1 ± 0.05	0.2 ± 0.02
R	2 ± 0.05	0.2 ± 0.22

Details of the polymers prepared, and to which test each was subjected, are given in Tables 1-4 APPENDIX III.

4:22. MONOMER CONVERSION.

For each series of polymer blends and polycaprolactam homopolymers the amount of monomer converted to polymer was determined by extracting shavings of the polymers with water in a soxhlet extraction apparatus. The results shown in Tables 29 and 30 are the average of at least two determinations.

TABLE 29.

MONOMER CONVERSION - POLYMER BLENDS.

No.	% SECOND COMPONENT IN BLEND	SECOND COMPONENT IN THE BLEND	% MONOMER CONVERTED TO POLYMER
S4	5.0	POLYSTYRENE	94.69
T1	5.0		95.47
U5	10.0		95.16
V3	15.0		94.38
W3	5.0	IMPACT STYRENE	94.57
X2	5.0		94.93
Y7	10.0		95.06
Z5	15.0		95.56
AA5	5.0	THERMOPLASTIC RUBBER	93.05
BB1	10.0		92.43
CC4	15.0		91.66

TABLE 30.

MONOMER CONVERSION - POLYCAPROLACTAM HOMOPOLYMERS.

No.	% MONOMER CONVERTED TO POLYMER.
N1	95.83
P1	94.94
Q3	96.49
R5	94.61.

Before the physical properties of the polymer blends and

polycaprolactam homopolymers were determined the amount of monomer converted to polymer was calculated.
For all the polycaprolactam homopolymers the conversion of monomer is high, but slightly better for the polymers prepared with the lower catalyst concentration. This can readily be explained in terms of degradation reactions discussed in the mechanism of the anionic polymerisation of caprolactam (Appendix 1). For the blends with polystyrene and impact styrene the results are almost the same and similar to those for the homopolymers. There is no apparent decrease in the conversion of monomer as the concentration of the second component in the blends is increased. The conversion of monomer for the polycaprolactam-thermoplastic rubber blends is lower than for the other blends and decreases as the amount of the second component in the blend is increased. Before the blends were moulded they were extracted with water in a soxhlet extraction apparatus for 24 hours. After the polymer blends and nylon 6 homopolymers had been moulded representative samples were analysed by differential thermal analysis and showed no trace of monomer.

4:22.2 THERMAL ANALYSIS.

The crystalline melting points of the polycaprolactam components of the polymer blends and the nylon 6 homopolymers are given in Tables 31 and 32.

TABLE 31.

CRYSTALLINE MELTING POINTS OF THE POLYCAPROLACTAM COMPONENTS OF THE POLYMER BLENDS.

POLYMER SERIES	CATALYST CONCENTRATION (MOLE %)	SECOND COMPONENT IN BLEND	% SECOND COMPONENT IN BLEND	CRYSTALLINE MELTING POINT (°C)
T	2.0	POLYSTYRENE	5	223
U			10	220
V			15	220
X	2.0	IMPACT STYRENE	5	223
Y			10	219
Z			15	219
AA	2.0	THERMOPLASTIC RUBBER	5	221
BB			10	220
CC			15	217

TABLE 32.

CRYSTALLINE MELTING POINTS OF THE POLYCAPROLACTAM HOMOPOLYMERS.

POLYMER SERIES	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE %)	CRYSTALLINE MELTING POINT (°C)
N	1.0	0.11	225°C
P	2.0	0.11	225°C
Q	1.0	0.21	225°C
R	2.0	0.21	225°C

The shape of the melting **endo**therms for the polymer blends are similar to those of the copolymers, and those for the polycaprolactam homopolymers are similar to that of the commercial nylon 6. Again the important information gained from the thermal analysis is the crystalline melting points of the polycaprolactam homopolymers and the polycaprolactam components of the blends. The melting points quoted in Tables 31 and 32 are the lowest points of the melting **endo**therms. The only indication of a second component in the blends from the thermal analysis is the shape of their melting **endo**therms. The melting **endo**therms of the polycaprolactam in the blends are broad while those for the polycaprolactam homopolymers are sharp. The temperature range of the melting **endo**therms of the blends is 14-18°C, compared with 6 degrees for the homopolymers. The melting points of the polycaprolactam components of the blends are a little lower than those of the homopolymers and decrease slightly as the concentration of the second component in the blend is increased.

For the blends with polystyrene there is no indication of a glass transition temperature around 100°C for either the moulded or unmoulded samples. This is because the polystyrene forms the dispersed phase of the blend and the polycaprolactam component has such a high melting point compared with the glass transition of the polystyrene.

The broad melting **endo**therm for the polymer blends is due to the second component which causes a large distribution in the polycaprolatam crystallite size. The incompatibility of the second component might interfere with the crystallisation which will in turn affect the melting point.

Taking into consideration the sample weights, the area enclosed by the melting endotherms indicates that the degree of crystallinity of the homopolymers is slightly greater than that for the polycaprolactam components of the blends.

4.22.3 APPEARANCE OF THE POLYMER BLENDS AND HOMOPOLYMERS.

As the amount of the second component in the blends was increased. their appearance gave the impression that the components were becoming more incompatible. The appearance of a particular blend depended on the second component, and also on its concentration.

When the concentration of the second component was 5% by weight blends prepared with polystyrene and impact styrene were similar in appearance and much better than those prepared with the thermoplastic rubber. In fact the appearance of these blends was almost as good as that of the polycaprolactam homopolymers, As the concentration of the second component was increased to 10% by weight the blends with polystyrene and impact styrene were just beginning to show signs of incompatibility. For the blends with the thermoplastic rubber there were definite signs of incompatibility. When the concentration of the second component was increased to 15% by weight the surface appearance of the blends containing the thermoplastic rubber were very rough and heterogeneous. There were also definite signs of incompatibility for the blends with polystyrene and impact styrene. The change in the appearance of the polymer blends was greater when the concentration of the second component was increased from 10 to 15%.

When the blends were moulded their surface appearance became rougher and more heterogeneous as the concentration of the second component was increased. Because of the high conversion of monomer in the blends with polystyrene and impact styrene they were moulded without extraction with water. No improvement in the surface appearance of the moulded polymers was obtained by extracting the last traces of unreacted monomer. On the other hand the appearance of the blends with the thermoplastic rubber were slightly improved by extracting the unreacted monomer and low molecular polymer before moulding.

The appearance of all the polycaprolactam homopolymers was good and, after moulding, it was difficult to tell them from the commercial nylon 6.

4:23 OPTICAL MICROSCOPY.

Section of the polymer blends were prepared and photographed and the results are shown in plates 10-17. Although all the plates are of polycaprolactam-impact styrene blends sections of the other blends were very similar. Some details of the plates are given in Table 33.

TABLE 33.

PLATE NUMBER	STATE (MOULDED/ UNMOULDED)	% SECOND COMPONENT IN BLEND (IMPACT STYRENE)	MAGNIFICATION X	MODE.
10	UNMOULDED	5	64	CROSS POLARS (CP)
11	UNMOULDED	5	64	PHASE CONTRAST (PH
12	UNMOULDED	5	160	PH
13	UNMOULDED	10	64	PH
14	MOULDED	5	64	PH
15	MOULDED	10	400	PH
16	MOULDED	5	400	PH
17	MOULDED	5	400	CP

The plates of the polycaprolactam-impact styrene blends will be discussed and, where they differ from the other blends, reference will be made.

Plates 10-13 are of unmoulded samples taken under phase contract and cross polar illumination at different magnifications. Plates 10,11 and 13, which were taken at low magnification, give an overall view of sections of the blends. They show that, when caprolactam is polymerised in the presence of impact styrene it does not form two distinct phases as might have been expected. Instead there is a continuous polycaprolactam phase which contains two kinds of particles. The first are impact styrene particles, usually small in size (1 to 6μ), the second are impact styrene "particles" which contain polycaprolactam. The dispersed phase particles vary in size (1 to 15μ) and both types of particles are randomly distributed in the polycaprolactam. Plate 12 is a section of photograph 11 taken at higher magnification and shows the polycaprolactam surrounded by impact styrene. It is interesting to note that during the preparation of impact styrene by the polymerisation of styrene monomer in the presence of dissolved rubber a similar phase structure is obtained.[113] There is however, a fundamental difference between the impact styrene system and the polymerisation of caprolactam in the presence of dissolved polymers. In the former some copolymerisation occurs which produces good adhesion between the components of the blend. That this does not occur with the polycaprolactam-impact styrene blends is illustrated by plate 13.

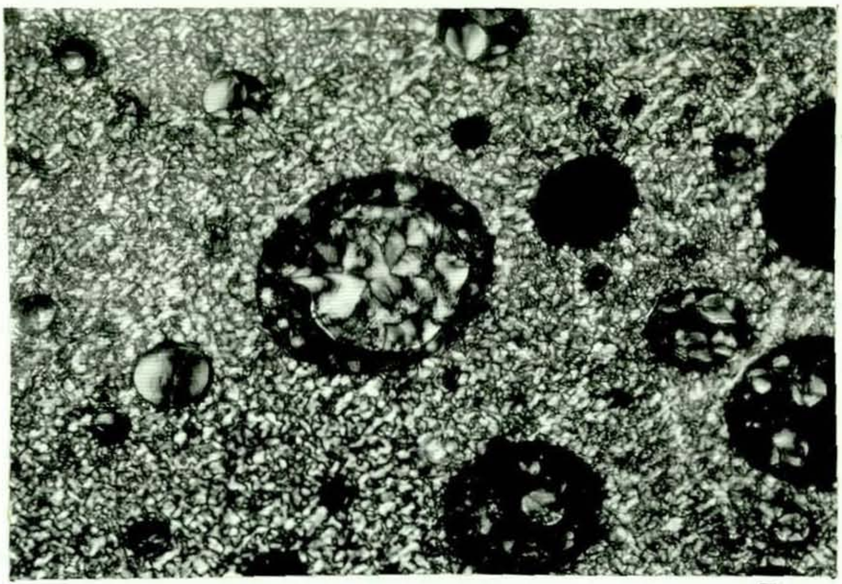


Plate 10
Polymer Blend Containing
5% Impact Styrene

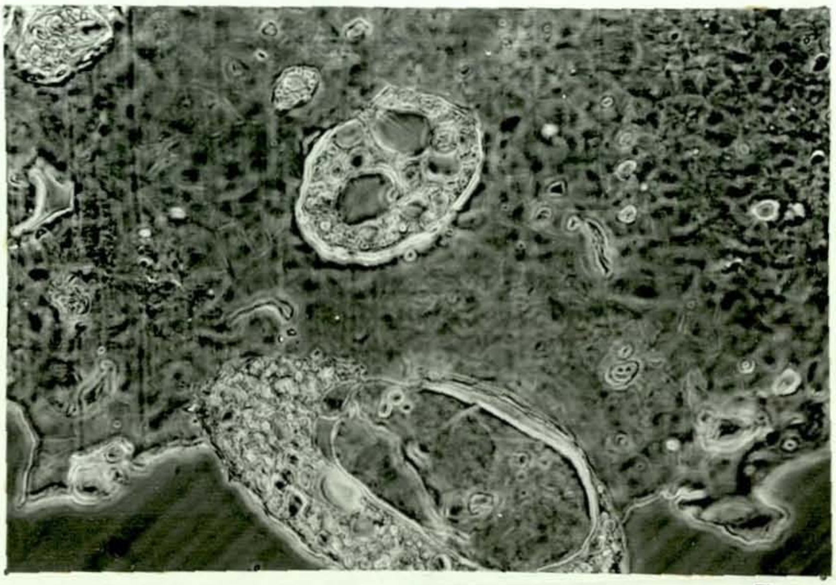


Plate 11
Polymer Blend Containing
5% Impact Styrene

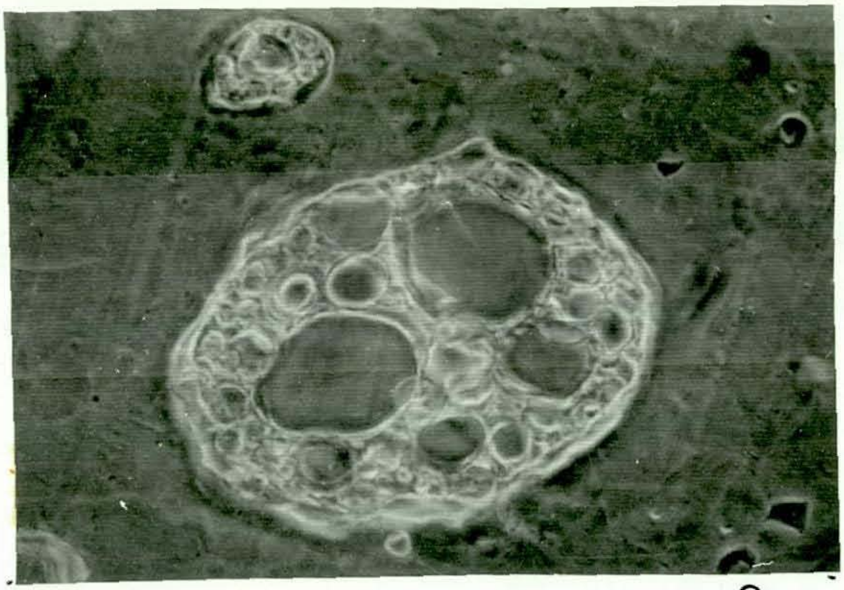


Plate 12
Polymer Blend Containing
5% Impact Styrene

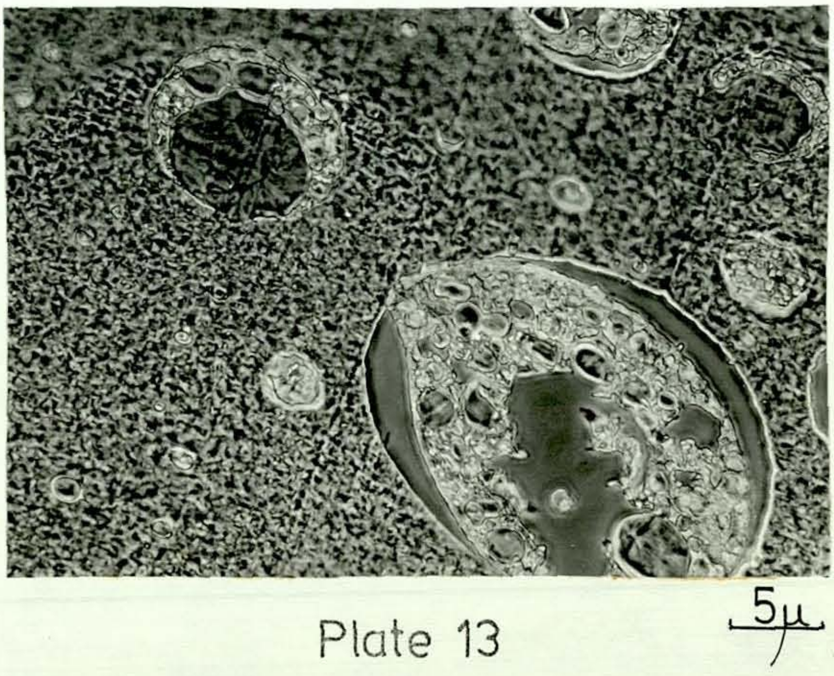


Plate 13
Polymer Blend Containing
10% Impact Styrene

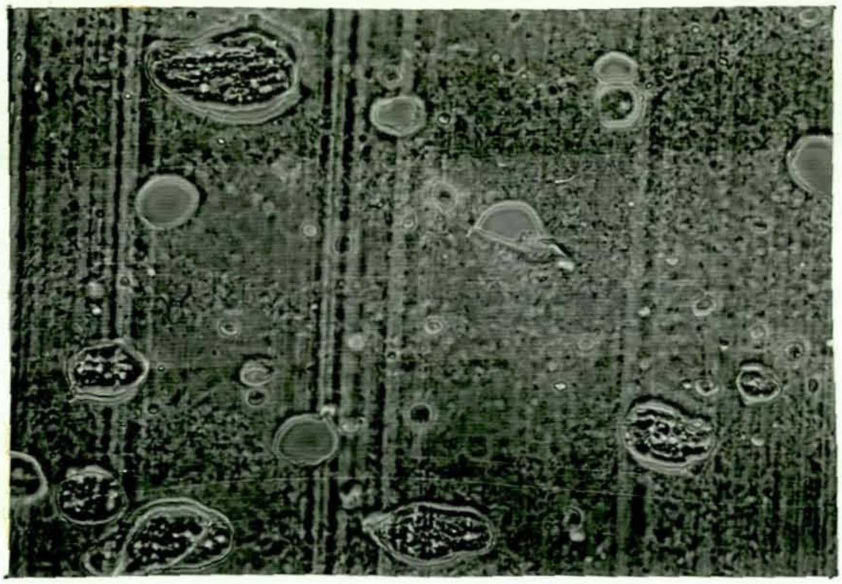


Plate 14

Polymer Blend Containing

5% Impact Styrene

Plate 15

Polymer Blend Containing

10% Impact Styrene

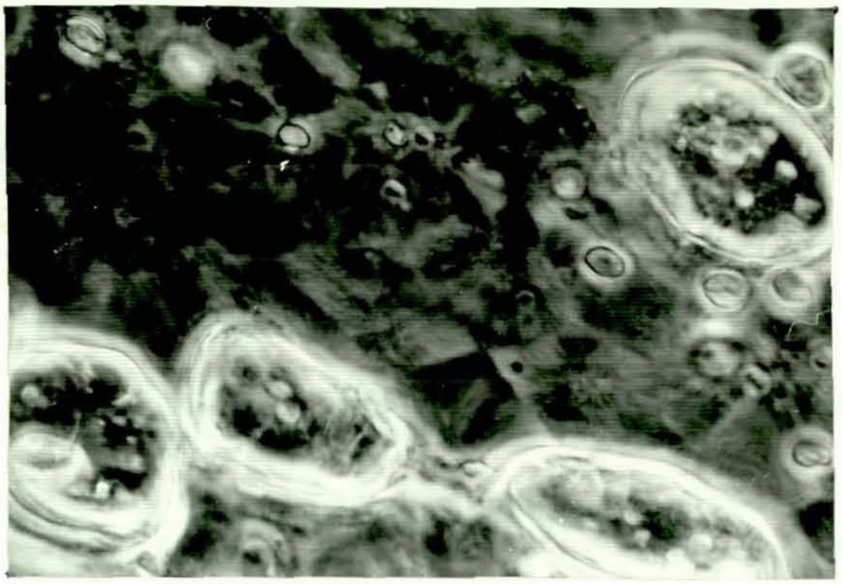


Plate 16
Polymer Blend Containing
5% Impact Styrene

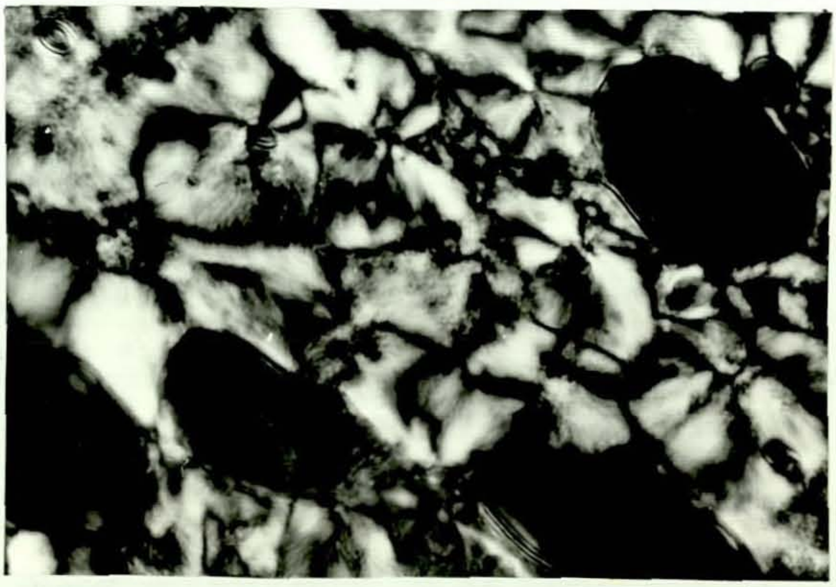


Plate 17
Polymer Blend Containing
5% Impact Styrene

During the preparation of the sections the two phases became separated because there were no interactions, such as hydrogen bonding, to hold them together. Separation also occurred in other sections examined and this observation helps to explain the deterioration in the physical properties of the blends as the concentrations of the second components are increased.

Plates 14-17 are of sections of moulded polymers taken under phase contrast and cross polar illumination at different magnifications. During the moulding process the components of the blend melt and form a more definite two phase structure. As expected polycaprolactam forms the continuous phase and impact styrene the dispersed phase. The dispersed phase particles vary in size and are randomly distributed. Plate 14, taken at low magnification, shows the variation and distribution of the dispersed phase particles and also shows that none contain polycaprolactam homopolymer. Plate 15, which is specific to the blends with impact styrene, is of a larger particle of impact styrene in a moulded polymer and clearly shows the crazes due to cutting the section. Plates 16 and 17 are of the same section taken under phase contrast and cross polar illumination respectively. Plate 16 shows some of the structure of the dispersed phase impact styrene and plate 17 shows the polycaprolactam crystallites. It is not as apparent from the plates of the moulded samples that the components of the blends are incompatible.

4:24 PHYSICAL PROPERTIES.

Some physical properties of the polymer blends were determined and compared with those of a commercial nylon 6 and polycaprolactam homopolymers prepared in the laboratory.

4:24.1 TENSILE STRESS-STRAIN PROPERTIES.

From each compression moulded sheet twenty dumbell test pieces were cut. Half were stored in a vacuum descicator over phosphorus pentoxide before testing, the remainder were allowed to come to equilibrium in a constant temperature room (23± 0.5°C 65% R.H). They were known as the "dry" and "equilibrated" samples respectively. The results for the polymer blends, polycaprolactam homopolymers and the commercial nylon 6 were calculated in exactly the same way as for the copolymers.

The tensile stress-strain results for the polycaprolactam homopolymers and the commercial nylon 6 are shown in Table 34. The "equilibrated" samples prepared with catalyst concentrations of 1 mole % elongated evenly but did not yield with necking. The homopolymers prepared with catalyst concentrations of 2 mole % yielded with necking, at similar stresses, but these were less than that of the commercial nylon 6.

The tensile strength at break for the homopolymers depended on the catalyst and cocatalyst concentrations. The homopolymers prepared with the lower catalyst and coatalyst concentrations had the greatest tensile strength at break. Increasing the catalyst concentration to 2 mole %, but keeping the lower cocatalayst concentration, resulted in a decrease in the tensile strength at break.

There was a greater decrease in the tensile strength at break when the catalyst concentration was kept at 1 mole % but the cocatalyst concentration was increased. The polymers prepared with the higher catalyst and cocatalyst concentrations had the lowest tensile strength at break. The tensile strength at break of the commercial nylon 6 was intermediate with those of the homopolymers prepared in the laboratory.

The elongations at break for the polycaprolactam homopolymers and the commercial nylon 6 follow a similar pattern to the tensile strength at break results.

For the "dry" samples, which yielded with necking, it was only possible to determine the yield strengths and elongations at break. The homopolymers prepared with the lower catalyst and cocatalyst concentrations had the highest yield strength. Increasing either the catalyst or cocatalyst concentration resulted in a decrease in the yield strength. The biggest decrease was observed when the catalyst concentration was increased. For homopolymers prepared with higher catalyst concentrations there was no apparent change in the yield strength as the cocatalyst concentration was increased. The commercial nylon 6 had a yield strength similar to that of the polycaprolactam homopolymers prepared with the lower catalyst and cocatalyst concentrations.

The polycaprolactam homopolymers prepared with the lower catalyst concentrations had higher elongations at break than those prepared with the higher catalyst concentrations.

Increasing the cocatalyst concentration resulted in a decrease in the elongation at break. The elongation at break for the commercial nylon 6 was between the values for the polycaprolactam homopolymers prepared with the higher catalyst concentration.

Table 35 shows the tensile stress-strain results for the polymer blends prepared with the higher catalyst and cocatalyst concentrations, together with the appropriate polycaprolactam homopolymer.

Under test conditions all the "equilibrated" samples of the polymer blends elongated but did not yield with necking.

Blends containing 5% polystyrene or impact styrene had tensile strengths at break which were similar to the polycaprolactam homopolymer. All other blends had tensile strengths at break which were less than that of the homopolymer. As the concentration of the second component in the blend was increased the tensile strength at break decreased. At the concentrations considered blends with polystyrene and impact styrene had similar tensile strengths at break. For a particular concentration of the second components, blends containing thermoplastic rubber had the lowest tensile strength at break.

The elongation at break results follow a similar pattern to the tensile strength at break results.

TABLE 34.

TENSILE PROPERTIES : POLYCAPROLACTAM HOMOPOLYMERS.

			"EQUILIBRATED" SAMPLES.			"DRY" SAMPLES.	
No.	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE %)	YIELD STRENGTH (MN/Sq m)	TENSILE STRENGTH AT BREAK (MN/Sq m)	ELONGATION AT BREAK (%)	YIELD STRENGTH (MN/Sq m)	ELONGATION AT BREAK (%)
N5	0.98	0.10	-	76.56	334	79.04	226
N6	0.98	0.11	-	73.11	319	80.54	227
N7	1.01	0.10	-	74.96	307	85.15	187
P4	1.98	0.11	-	57.20	289	51.95	195
P7	2.01	0.11	-	55.93	263	49.02	182
Q1	1.02	0.21	39.12	62.23	275	75.65	147
Q4	0.98	0.21	34.94	69.87	285	71.96	172
R1	1.99	0.21	37.06	46.59	190	66.26	41
R3	2.03	0.21	38.06	42.35	154	81.99	12
N6/1	-	-	44.69	54.92	204	82.15	59
N6/2	-	-	43.84	67.28	306	83.04	84

TABLE 35

TENSILE PROPERTIES OF POLYMER BLENDS.

CATALYST CONCENTRATION 2 mole %.

POLYMER	% SECOND COMPONENT IN BLEND	No.	"EQUILIBRATED" SAMPLES			"DRY" SAMPLES.	
			YIELD STRENGTH (MN/Sq m)	TENSILE STRENGTH AT BREAK (MN/Sq m)	ELONGATION AT BREAK (%)	YIELD STRENGTH (MN/Sq m)	ELONGATION AT BREAK (%)
POLYCAPROLACTAM HOMOPOLYMER	-	R1	37.06	46.59	190	66.26	41
		R3	38.06	42.35	154	81.99	12
POLYSTYRENE/ POLYCAPROLACTAM POLYMER BLENDS	5	T2	-	43.19	173	63.75	99
	10	U3	-	33.45	86	46.92	14
		U4	-	39.14	172	53.88	19
	15	V1		28.73	55	46.27	11
IMPACT STYRENE/ POLYCAPROLACTAM POLYMER BLENDS	5	X1	-	44.04	186	68.46	14
	10	Y1	-	34.46	147	52.10	15
		Y4	-	34.71	122	53.51	14
	15	Z3	-	30.22	110	49.68	12
		Z4	-	33.03	63	47.38	11
THERMOPLASTIC RUBBER/ POLYCAPROLACTAM POLYMER BLENDS	5	AA3	-	34.80	83	53.79	20
		AA4	-	39.54	116	58.83	23
	10	BB4	-	21.57	49	33.71	17
		BB5	-	23.30	30	35.93	10
	15	CC1	-	14.93	21	19.26	7

TABLE 36.

TENSILE PROPERTIES OF POLYMER BLENDS.

CATALYST CONCENTRATION 1 MOLE %.

			"EQUILIBATED" SAMPLES.		"DRY" SAMPLES.	
POLYMER	% SECOND COMPONENT IN BLEND	No.	TENSILE STRENGTH AT BREAK (MN/Sq m)	ELONGATION AT BREAK (%)	YIELD STRENGTH (MN/Sq m)	ELONGATION AT BREAK (%)
POLYCAPROLACTAM HOMOPOLYMER	-	N5	76.56	334	79.04	226
		N6	73.11	319	80.54	227
		N7	74.96	307	85.15	187
POLYSTYRENE/ POLYCAPROLACTAM POLYMER BLENDS	5	S1	63.43	311	62.25	168
IMPACT STYRENE/ POLYCAPROLACTAM POLYMER BLENDS	5	W1	47.05	237	55.89	79

For the "dry"samples, which again yielded with necking, it was only possible to measure the yield strength and the elongation at break.

The blends containing 5% polystyrene or impact styrene had similar yield strengthsto the polycaprolactam homopolymer. The yield strengths of all the blends decreased as the concentration of the second component was increased. Blends with polystyrene and impact styrene had similar yield strengths which, at the concentrations of the second component considered, were greater than those for blends with the thermoplastic rubber.

The elongations at break for the polycaprolactam homopolymer and the polymer blends were similar.

Table 36 shows the tensile stress-strain results for the polymer blends and polycaprolactam homopolymer prepared with the lower catalyst and cocatalyst concentrations.

Under test conditions the "equilibrated" samples elongated but did not yield with necking. The polycaprolactam homopolymer had a greater tensile strength at break than the polymer blends. The blend with polystyrene had a greater tensile strength at break than that with impact styrene. The elongation at break results followed a similar pattern to the tensile strength at break results.

For "dry" samples it was again only possible to measure yield strengths and elongations at break. The yield strengths of the blends were less than that of the homopolymer. The blend with polystyrene had a greateryield strength than the blend with impact styrene.

The homopolymer had the greatest elongation at break, the value for the blend with polystyrene being greater than that with impact styrene.

The tensile stress-strain curves obtained from "equilibrated" samples of the polymer blends and polycaprolactam homopolymers are shown in Figures 17 and 18 respectively.

Figure 17 shows a typical curve for test pieces which elongated evenly but did not yield with necking. Polymers which gave this type of stress-strain curve were the polycaprolactam homopolymers prepared with catalyst concentrations of 1 mole % and all the polymer blends. When the test pieces were subjected to a tensile stress the whole of the test area elongated in a uniform manner until they broke. Test pieces from polymers with poor tensile properties had broken before they had elongated to point A, those with better tensile properties broke between points A and B.

Figure 18 shows a typical curve for polycaprolactam homopolymers prepared with catalyst concentrations of 2 mole %. When test pieces of these polymers were subjected to a tensile stress they yielded, point A, and then elongated by drawing towards one of the jaws. Polymers prepared with the higher cocatalyst concentration usually broke before they had elongated to point B, the point where the width of the dumbell test piece started to increase. When test pieces of the polymers prepared with the lower cocatalyst concentration reached this point there was a slight increase in the stress before they "yielded" again, point C.

FIGURE 17

TENSILE STRESS-STRAIN CURVE

Polymer Blends With Polycaprolactam And Polycaprolactam Homopolymers Prepared With A Catalyst Concentration Of 1 Mole % "Equilibrated" Samples

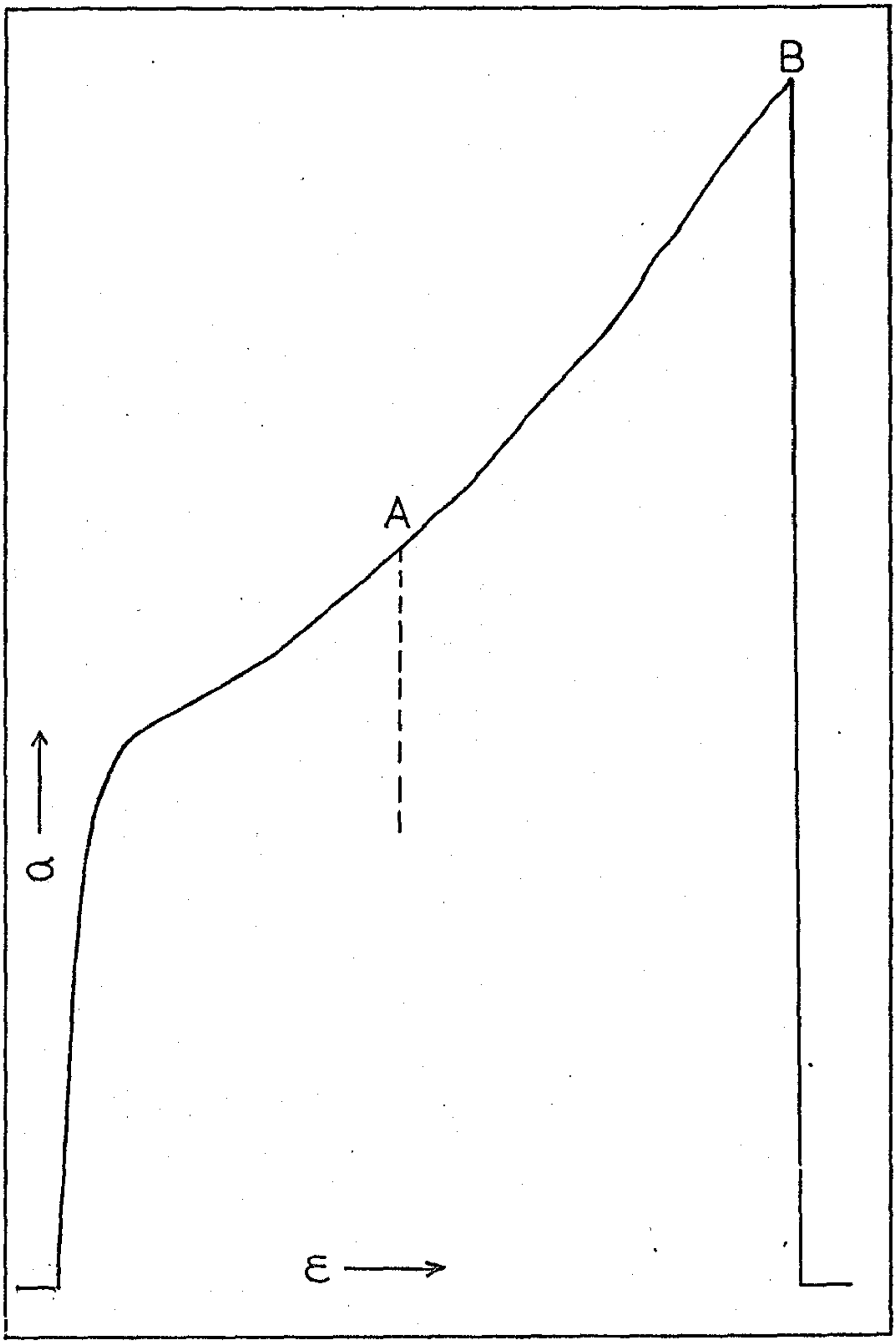
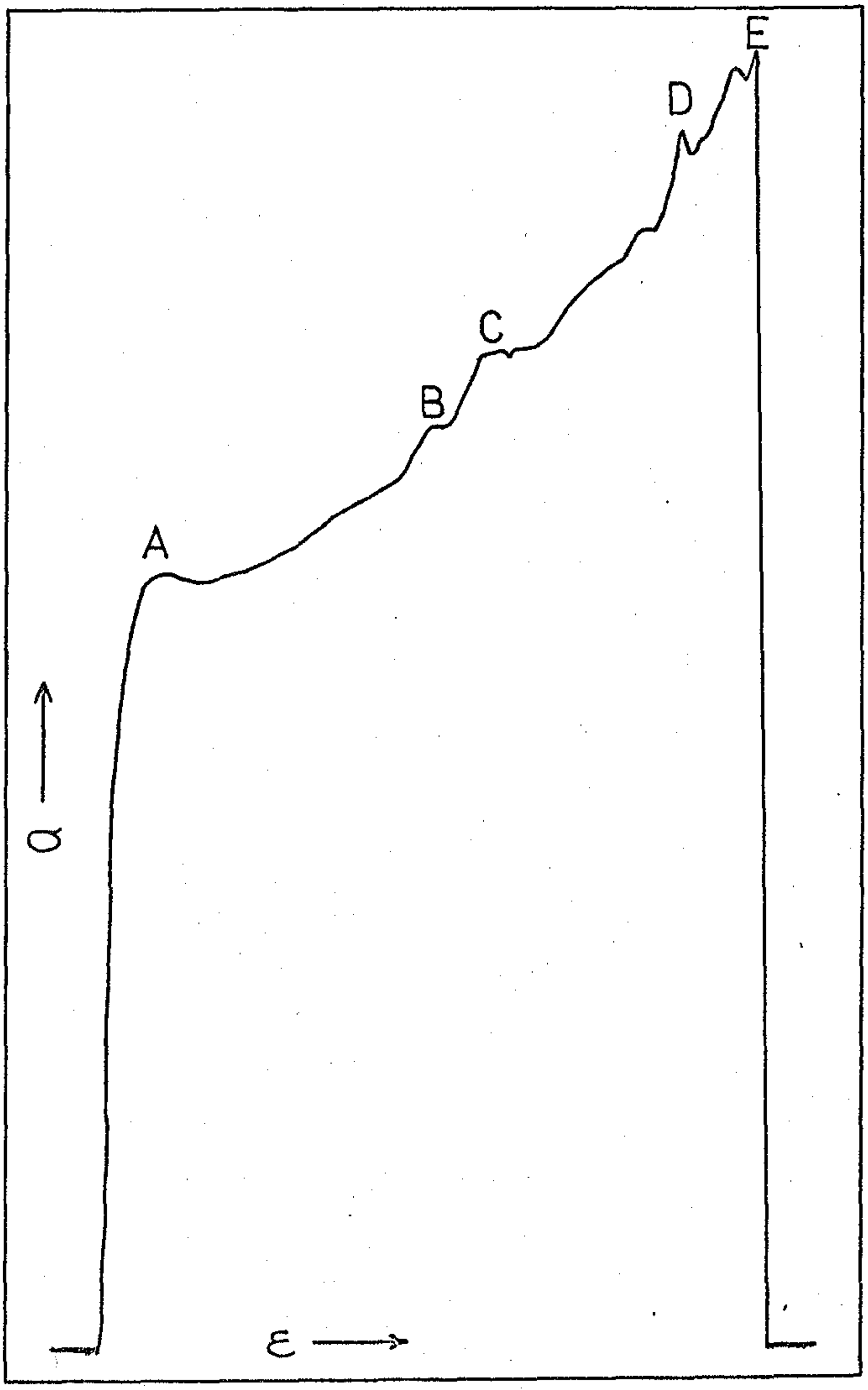


FIGURE 18

TENSILE STRESS-STRAIN CURVE

Polycaprolactam Homopolymers Prepared
With A Catalyst Concentration Of 2 Mole%
"Equilibrated" Samples



The test pieces then elongated by drawing towards the opposite jaw until they broke or the test area had become fully extended. When the whole of the test area had become fully extended the test pieces either broke, or "yielded" again, point D, before finally breaking, point E. Test pieces which "yielded" more than once only elongated a few percent more before breaking.

The tensile stress-strain curves for "dry" samples of the homopolymers and polymer blends are shown in Figures 19,20 and 21.

The curves for "dry" samples of all the polycaprolactam homopolymers, except those prepared with the higher catalyst and cocatalyst concentrations, are shown in Figure 19 and are similar to those described for the copolymers (page 148). The average elongations at break given in Table 34 gives an indication of the types of curves to expect for polymers prepared with the various catalyst and cocatalyst concentrations. Test pieces of polymers with good elongations at break broke in similar positions to those of the copolymers. Polymers with poor elongations at break usually broke before the test pieces had elongated to point B.

Figure 20 shows a typical curve for the polycaprolactam homopolymers prepared with the higher catalyst and cocatalyst concentrations. The yield points (point A) for these polymers were never as sharp as those for the other homopolymers and the samples always broke before they had elongated to the point where the width of the test piece started to increase. Most of the test pieces broke as they were elongating by drawing towards one of the jaws, point B.

FIGURE 19

TENSILE STRESS-STRAIN CURVE

Polycaprolactam Homopolymers

"Dry" Samples

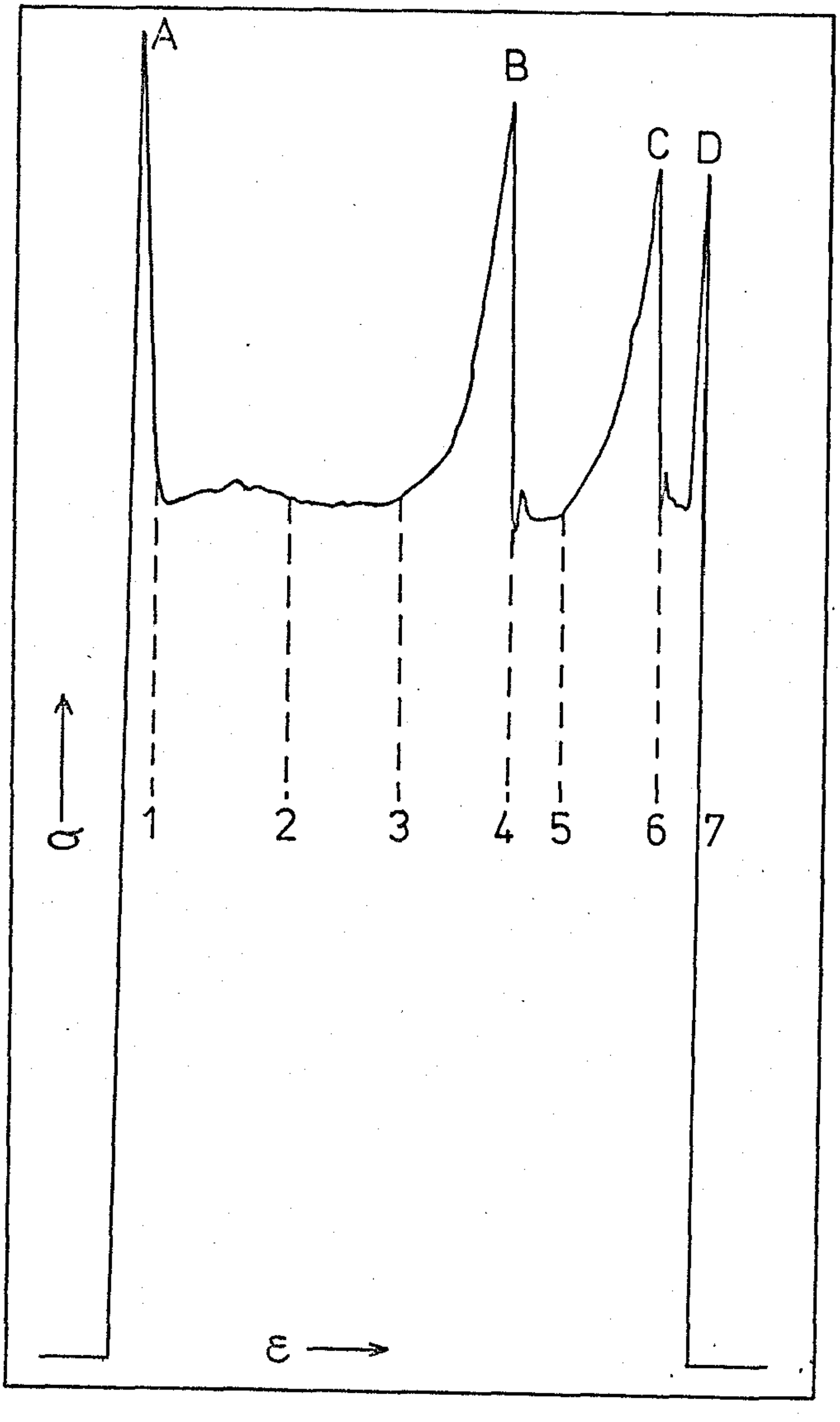


FIGURE 20

Polycaprolactam Homopolymers Prepared With High Catalyst And Cocatalyst Concentrations

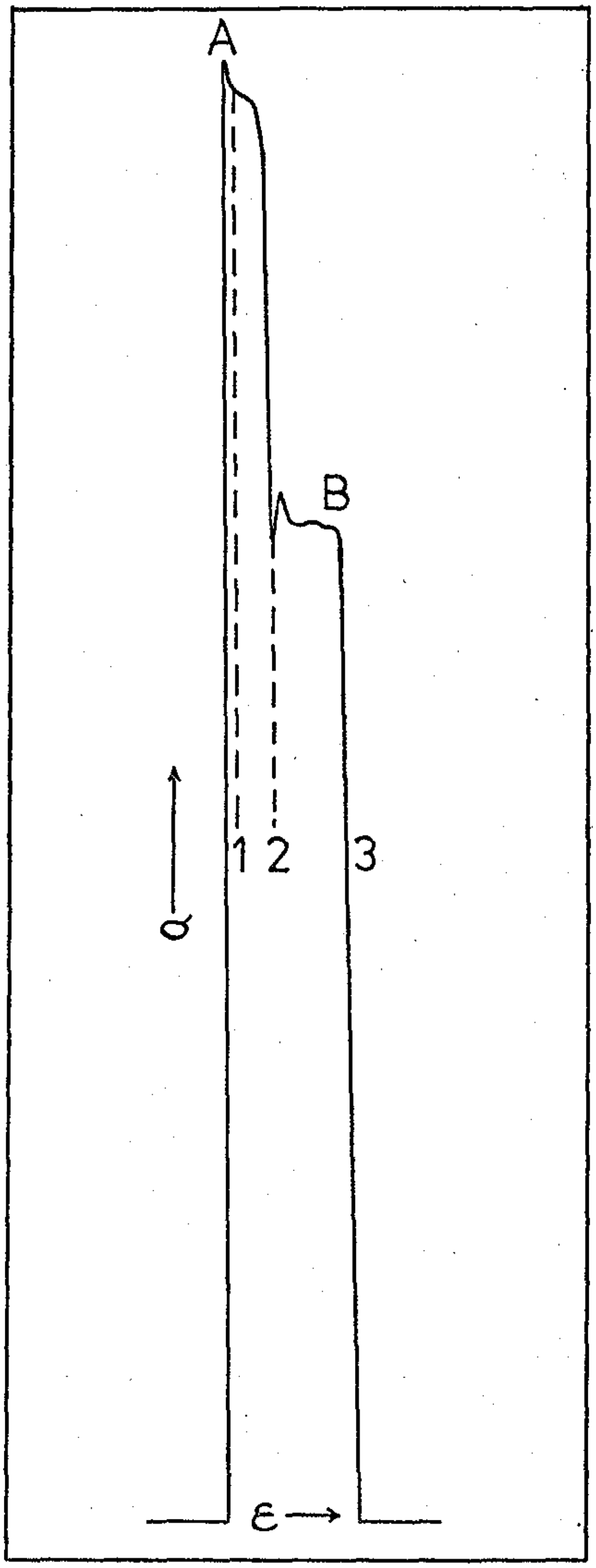
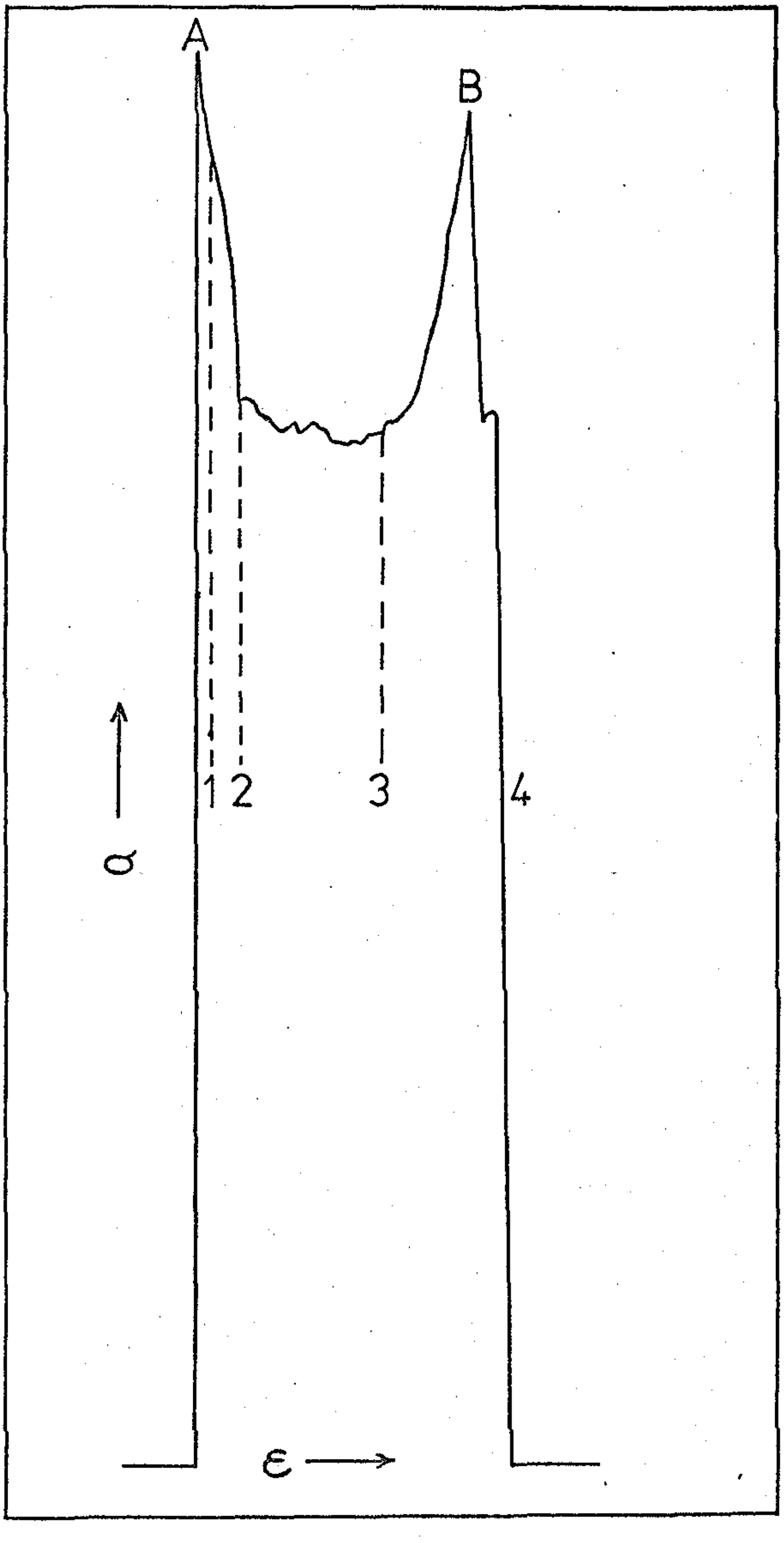


FIGURE 21

Polymer Blends With Polycaprolactam

"Dry" Samples



The stress-strain curve shown in Figure 21 contains features of all the different types of curves obtained for the polymer blends. Figure 21 is in fact a typical curve for blends containing 5% polystyrene or impact styrene. Although the yield point, point A, is not as sharp as for the homopolymers shown in Figure 19 the remainder of the curve is similar to point B and the polymers were elongating in a similar manner. The test pieces for these blends usually broke at points 3 or 4. Blends containing 10 and 15% polystyrene or impact styrene and all the blends containing thermoplastic rubber had poor tensile properties and broke as soon as they had yielded, or shortly afterwards, points 1 and 2.

The results show that the catalyst and cocatalyst concentrations have a significant effect on the tensile properties of the polycaprolactam homopolymers and the polymer blends. The properties of the blends are also affected by the particular second component and its concentration. The tensile stress-strain curves give an indication of the crystallite structure of the polycaprolactam homopolymers and the polycaprolactam components of the blends.

When test pieces of the homopolymers prepared with the lower catalyst concentration are subjected to a tensile stress they elongate in a uniform manner but do not yield with necking. The homopolymers prepared with the lower catalyst and cocatalyst concentrations have the highest molecular weight and best tensile properties.

When the cocatalyst concentration is increased lower molecular weight polymers with broader molecular weight distributions are formed and this has an adverse affect on their tensile properties. Increasing the cocatalyst concentration makes initiation more efficient so that no very high molecular weight molecules are formed.

Test pieces of the homopolymers prepared with the higher catalyst concentration yielded with necking, and then elongated by drawing when subjected to increasing tensile stress. As the reaction mechanism is dependent on the formation of lactam anions an increase in the catalyst concentration will mean that more are formed and lower molecular weight polymer will result. As expected, an increase in the cocatalyst concentration has an adverse affect on the tensile properties.

The shape of the stress-strain curves indicates that it is easier to elongate the higher molecular weight homopolymers. It is easier to pull the molecules out of the crystallites so that the test pieces do not yield with necking when a tensile stress is applied. Because of their high molecular weight the polymers have good elongations and tensile strengths at break.

The values given in Table 34 are only apparent tensile strengths at break because they do not take into consideration changes in the cross sectional area of the test pieces as they elongate. The true tensile properties of the higher molecular weight polymers are therefore better than the table indicates. The homopolymers prepared with the higher cocatalyst concentrations do not have such good properties because there are no really long polymer chains to connect the shorter ones when the polymers are elongating.

In polymers prepared with the higher catalyst concentration there are more "tie" molecules and a higher stress is required to pull the molecules out of the crystallites. This is why the test pieces yield when subjected to a tensile stress. As the stress-strain curves are not smooth it indicates that even when the test pieces are elongating by drawing the molecules do not pull uniformly out of crystallites.

A plot of the true tensile stress against elongation can give an indication of the crystallite structure of the polymers. If it is easy to pull molecules out of the crystallites test pieces will not yield with necking when subjected to a tensile stress. Figure 17 shows a typical stress-strain curve for such polymers. For such polymers it would be expected that a plot of the true tensile stress against elongation will be such that a tangent cannot be drawn to any part of the curve. For polymers which yield with necking and then elongate by drawing it would be expected that a tangent could be drawn, from the -1 point on the negative strain axis (Considire's construction)[114,115] to a point on the curve of the true stress against elongation. A typical stress-strain curve for this type of polymer is shown in Figure 18. An attempt was made to plot these curves but was only partially successful because the scale for the elongation is not linear.

The results show that drying has an adverse affect on the tensile properties of all the homopolymers. The shapes of the tensile curves indicates that for all the homopolymers it is difficult to pull the molecules out of the crystallites and all yield with necking when subjected to a tensile stress.

Figure 20 indicates that for the homopolymers prepared with the higher catalyst and cocatalyst concentrations more "tie" molecules must be broken and as a result these polymers do not have sharp yield points. Removing the water, which acts as a plasticiser, has the greatest effect on these polymers and they have very poor tensile properties when dry. As expected, the high molecular weight polymers have the best tensile properties because the long polymer chains can still extend a considerable distance before breaking, even in the absence of water.

None of the "equilibrated" samples of the polymer blends prepared with the higher catalyst and cocatalyst concentrations yielded with necking when subjected to a tensile stress. Instead they elongated uniformly over the whole of the test area in a manner similar to that of the homopolymers prepared with the lower catalyst concentration. The introduction of a second component into polycaprolactam causes a reduction in the degree of crystallinity but this alone will not account for the observations. The second components of the blends must therefore affect the structure of the crystallites in such a way that there is a reduction in the number of "tie" molecules. There must be a reduction in the number of such links if the molecules are to be pulled easily out of the crystallites.

None of the blends had tensile strengths and elongations at break as high as those of the corresponding homopolymer. The reason for this is that the second components of the blends, though soluble in and compatible with caprolactam, are incompatible with polycaprolactam.

There is evidence that there are no physical bonds such as polar forces or hydrogen bonds acting between the two phases. Optical microscopy shows that cutting samples on a microtone can cause phase separation and that during the moulding process a more definite two phase structure is formed. There are no chemical bonds between the two components of the blends because no copolymerisation occurs during their preparation. This is shown by the fact that all the second component can be extracted from the polycaprolactam by the use of suitable solvents. An increase in the concentration of the second component in the blends therefore has an adverse effect on their tensile properties. At the various concentrations of the second component considered the tensile properties of the blends with polystyrene and impact styrene are similar, and better those with the thermoplastic rubber. As the butadiene in the impact styrene is partially cross linked its incompatibility with polycaprolactam is reduced so that there is little difference between it and polystyrene at concentrations up to 15% by weight. The butadiene in the thermoplastic rubber is not cross linked and though the polymer is soluble in caprolactam, it is incompatible with polycaprolactam.

The results for the blends prepared with the lower catalyst and cocatalyst concentrations are noticeably different from those described above. Introducing a second component into high molecular weight polycaprolactam has a definite adverse affect, even at concentrations of 5% by weight. There is also a difference between blends with polystyrene and impact styrene, those with polystyrene having the better properties in the present context.

This difference could be due in part to the fact that the tensile properties of polystyrene are better than those of impact styrene. Even though the second component has an adverse effect on the tensile properties of the blends they still have better properties than those prepared with the higher catalyst and cocatalyst concentrations. Although the polycaprolactam molecules pull easily out of the crystallites there comes a point when the strength of the blend depends on its second component and this is when they fail. In order to give better tensile properties than blends with impact styrane the polystyrene must be more compatible with the high molecular weight polycaprolactam. This is in addition to the better tensile properties of the polystyrene.

As expected, drying has an adverse affect on the tensile properties of the blends. The results indicate that the properties of the blends are affected by the removal of the plasticising water and the incompatibility of their components. Because polymer incompatibility has an adverse affect on their properties the blends are affected more than the homopolymers by drying.

Figure 21 would indicate that none of the blends show sharp yield points when subjected to a tensile stress but this is only partially true. Blends with the worst tensile properties snapped almost as soon as the test pieces had come under tension, those with slightly better properties often tore instead of snapping when they broke and this accounts for the shape of the stress-strain curve.

For blends with better tensile properties the yield points are not sharp and this is an indication of the difficulty in pulling molecules out of the crystallites. Once they have yielded the test pieces elongate by drawing until they fail at a weak point which may be due to the second component. This was often the point where the width of the test specimens started to increase and there was a change in the tensile stress situation.

4:24.2 IMPACT PROPERTIES.

From each compression moulded "slab" twelve test pieces were cut. All the test pieces from one polymer were either allowed to equilibrate in a constant temperature room (23 ± 0.5°C, 65% RH), or were stored in a vacuum descicator over phosphorus pentoxide. The samples were referred to as the "equilibrated" and "dry" samples respectively. The results were calculated in the same way as for the copolymers and are given in Tables 37-39.

TABLE 37.

IMPACT STRENGTHS OF POLYCAPROLACTAM HOMOPOLYMERS

"EQUILIBRATED" SAMPLES				"DRY" SAMPLES.			
No.	CATALYST CONCENTRATION (MOLE%)	COCATALYST CONCENTRATION (MOLE %)	CHARPY IMPACT STRENGTH (K JOULES/M^2 BEHIND NOTCH)	No.	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE %)	CHARPY IMPACT STRENGTH (K JOULES/M^2 BEHIND NOTCH)
N3	0.99	0.11	16.73	N2	1.01	0.11	4.68
N4	1.03	0.11	17.18	N8	1.00	0.11	4.40
P2	1.98	0.11	16.54	P5	2.01	0.11	4.94
P3	1.98	0.11	18.62	P6	1.99	0.11	5.08
Q6	1.02	0.21	15.64	Q2	1.02	0.21	3.56
Q7	0.98	0.21	16.02	Q5	0.99	0.21	3.58
R6	1.99	0.21	16.50	R2	2.03	0.21	3.43
R7	2.02	0.21	16.44	R4	2.03	0.21	3.49
N6/5	-	-	12.11	N6/3	-	-	5.26
N6/6	-	-	12.08	N6/4	-	-	5.31

TABLE 38.

IMPACT STRENGTHS OF POLYMER BLENDS.

CATALYST CONCENTRATION 2 MOLE %.

POLYMER	% SECOND COMPONENT IN BLENDS	"EQUILIBRATED" SAMPLES		"DRY" SAMPLES.	
		No.	CHARPY IMPACT STRENGTH (K JOULES/M^2 BEHIND NOTCH)	No.	CHARPY IMPACT STRENGTH (K JOULES/M^2 BEHIND NOTCH)
POLYCAPROLACTAM HOMOPOLYMER	-	R6	16.50	R2	3.43
	-	R7	16.44	R4	3.49
POLYSTYRENE/ POLYCAPROLACTAM POLYMER BLENDS.	5	T3	12.24	T5	2.55
		T4	13.08	T6	2.46
	10	U1	10.71		
		U2	10.40		
	15	V2	9.35		
		V4	9.84		
IMPACT STYRENE/ POLYCAPROLACTAM POLYMER BLENDS	5	X3	14.74	X5	2.46
		X4	11.37	X6	2.58
	10	Y2	9.71	Y5	2.36
		Y3	10.05	Y6	2.21
	15	Z1	8.14		
		Z2	7.90		
S.B.S.THERMO-PLASTIC RUBBER/ POLYCAPROLACTAM POLYMER BLENDS.	5	AA1	16.23		
		AA2	16.27		
	10	BB2	12.73		
		BB3	13.67		
	15	CC2	11.52		
		CC3	11.74		

TABLE 39.

IMPACT STRENGTHS OF POLYMER BLENDS.

CATALYST CONCENTRATION 1 MOLE %.

		"EQUILIBRATED" SAMPLES.		"DRY"SAMPLES.	
POLYMER	% SECOND COMPONENT IN BLEND	No.	CHARPY IMPACT STRENGTH K JOULES/M^2	No.	CHARPY IMPACT STRENGTH K JOULES M/^{2}
POLYCAPROLACTAM HOMOPOLYMERS	-	N3	16.73	N2	4.98
		N4	17.18	N8	4.66
POLYSTYRENE/ POLYCAPROLACTAM POLYMER BLENDS	5	S5	15.84	S2	5.19
		S6	16.07	S3	5.14
IMPACT STYRENE/ POLYCAPROLACTAM POLYMER BLENDS	5	W4	15.98	W2	5.05
		W5	15.67	W6	4.92

The impact properties of the polycaprolactam homopolymers and the commercial nylon 6 are shown in Table 37.

For the "equilibrated" samples the impact strengths of the polycaprolactam homopolymers were similar, and better than that of the commercial nylon 6. The catalyst and cocatalyst concentrations appeared to have little effect on the impact properties of the homopolymers.

For the "dry" samples the impact strength of the commercial nylon 6 was greater than that for all the polycaprolactam homopolymers. The homopolymers prepared with catalyst concentrations of 1 mole % had greater impact strengths than those prepared with catalyst concentrations of 2 mole %. The cocatalyst concentration appeared to have little effect on the impact strengths of the homopolymers.

The impact strengths of the polymer blends and polycaprolactam homopolymer prepared with the higher catalyst and cocatalyst concentrations are given in Table 38.

For the "equilibrated" samples the results show that, of the blends, those with the thermoplastic rubber had the best impact properties. The blends prepared with 5% thermoplastic rubber had impact strengths which were similar to that of the polycaprolactam homopolymer. All the other polymer blends had impact strengths which were less than that of the homopolymer. The impact strength of the blends decreased as the concentration of the second component was increased.

At the concentrations of the second components considered, the blends with polystyrene and impact styrene had similar impact strengths.

For the "dry" samples only certain blends were tested. The impact strengths of the blends were less than that of the homopolymer. The blends with polystyrene and impact styrene had similar impact strengths when the concentration of the second component was 5%. For the blends with impact styrene the impact strength was decreased as the concentration of the second component was increased.

Table 39 shows the impact strengths of the blends prepared with the lower catalyst and cocatalyst concentration, together with the appropriate polycaprolactam homopolymer for comparison purposes. For the "equilibrated" samples the blends and homopolymer had similar impact strengths. For the "dry" samples the impact strengths of the blends were similar and better than that of the homopolymer.

The impact strengths of the "equilibrated" samples of the polycaprolactam homopolymers are similar and better than that of the commercial nylon 6. The major factor affecting the impact strengths of the homopolymers appears to be their degrees of crystallinity. Thermal analysis indicates that the degrees of crystallinity for the homopolymers are similar, and slightly greater than that of the commercial nylon 6. Changes in the molecular weight of the polymers has little effect on their impact properties.

Drying the polymers has a greater effect on the impact strengths of the polycaprolactam homopolymers than that of the commercial nylon 6. This is again due to the degree of crystallinity of the polymers, the commercial nylon6 has a slightly greater content of amorphous polymer and the best impact properties. All the homopolymers had poor impact properties after drying.

None of the "equilibrated" samples of the blends had impact properties which were as good as those of the corresponding polycaprolactam homopolymers.

Blends prepared with the lower catalyst and cocatalyst concentrations had properties which were almost as good as the corresponding homopolymer. The introduction of a second component to the extent of 5% by weight does not appear to reduce the degree of crystallinity of the polycaprolactam to any great extent, the slight decrease in the impact strength being due to polymer incompatibility. If the concentration of the second component were to be increased there would be a more noticeable reduction in the impact strength of the blends because of polymer incompatibility. Blends prepared with the higher catalyst and cocatalyst concentrations had impact properties which were inferior to those of the corresponding homopolymer. Increasing the concentration of the second component had an adverse affect on the impact properties of the blends. The second component appears to have greater effect on the degree of crystallinity of the lower molecular weight polycaprolactam and evidence to support this is obtained from thermal analysis of the blends.

Blends with thermoplastic rubber had better impact properties than those prepared with polystyrene or impact styrene. This is due to the superior impact properties of the thermoplastic rubber compared with those of the other two polymers, and partly offsets the decrease in impact strength of the blends due to polymer incompatibility. For all the series of polymer blends there is a decrease in the impact strength as the concentration of the second component is increased due to polymer incompatibility.

Some "dry" samples were tested in order to determine the effect of the second component on samples from which all traces of plasticising moisture had been removed.

Drying the polymers had an adverse effect on the impact properties of both the blends and the homopolymers. When the concentration of the second component is 5% it appears to have little effect on the impact properties of the blends. The decrease in impact properties is similar for both the polymer blends and homopolymers, whatever the catalyst and cocatalyst concentrations. It is expected that if the concentration of the second component in the blends were to be increased it would have an adverse affect on their impact properties compared with those of the homopolymers due to polymer incompatibility.

5: CONCLUSIONS.

The aim of this work was to extend the usefulness of polymers using the technique of polymerising a monomer in the presence of a dissolved polymer, a method which has proved successful for other systems. Copolymers with interesting properties have been prepared but attempts to prepare polymer blends have only been partially successful because of polymer incompatibility; however, such problems usually arise in any new work of this kind. Nevertheless, the selection of the unusual monomers in this thesis and the study of their polymerisation in the presence of other polymers has been shown to be a novel and interesting field of study.

The polymer solubility experiments showed that about one third of the polymers selected for study were soluble to an extent of 10% by weight in either caprolactam or laurolactam at 150°C. The results can be explained in terms of polymer solubility parameters, hydrogen bonding and polymer crystallisation. Although there are many factors affecting polymer solubility the value of the solubility parameter is a useful guide of the results to expect. There is, of course, a lack of accurate solubility data, especially for the newer homopolymers and copolymers, but it is hoped that this is only a temporary obstacle in the way of satisfactory systems. An indication of the value of the solubility parameter at 150°C for the polymers studied was obtained. [redacted]

As expected there was only a narrow range of values of the solubility parameter for which polymers were soluble in a given monomer.

Polymers soluble to an extent of 10% by weight were dissolved in the monomers which were then polymerised by an anionic mechanism. The method of polymerisation had to be varied slightly for some polymers because ~~the catalyst reacted with them more rapidly than it did with the monomer. For polymerisation to occur in these cases the lactam anions have to be formed in a separate vessel~~ polymerisation did not occur unless the lactam anions were formed in a separate vessel. At 150°C polysulphone and polycarbonate act as cocatalysts in the polymerisation of caprolactam with the formation of copolymers. Polymerising the monomers in the presence of other dissolved polymers results in distinctly heterogeneous polymer blends.

Polysulphone-polycaprolactam copolymers were prepared with various catalyst concentrations, polysulphone concentrations and polymerisation times. Experiments to determine copolymer composition, copolymer density and polymer solubility indicated that cleavage of the polysulphone molecule occured during the polymerisation. This was confirmed by experiments to determine the molecular weight of the polysulphone attached to the polycaprolactam.

A reaction mechanism explaining all the observations, and also in agreement with realted work was[71] proposed.

The physical properties of the copolymers measured indicated that they could be useful in fibre forming. The appearance of the copolymers after moulding showed them to have better heat resistance than nylon 6.

Polymer blends of polycaprolactam with polystyrene, impact styrene or SBS thermoplastic rubber are incompatible. Increasing the concentration of the second component in the blends was found to have an adverse effect on their physical properties, though it is not claimed that all the relevant technological factors have been studied.

Optical microscopy indicated that there is no adhesion between the components of these blends. Before moulding some of the dispersed phase particles contain polycaprolactam but moulding changes the polyphase structure to a definite two phase structure. This implies that no copolymerisation takes place under the conditions used.

The results agree with the observation of Bohn[17] that simple blends containing a crystalline homopolymer are incompatible.

6. SUGGESTIONS FOR FURTHER WORK.

6:1 POLYMER SOLUBILITY.

Polymer solubility parameters could be used to give an indication of polymer solubility for systems involving polymers and solvents or monomers. Unfortunately at present the data is scattered and few of the newer homo and copolymers have been studied. Also, the test methods used are such that it is difficult to compare results.

The most important requirement in order to take full advantage of the useful information polymer solubility parameters can provide is a standard test method. The test method should have a set procedure similar to those laid down by British Standards or A.S.T.M. The test method should take into account factors such as polymer molecular weight, copolymer composition, temperature and pressure, all of which affect the value of the solubility parameter to varying degrees. This work has indicated that polymer molecular weight has the major influence on the value of δ , the solubility parameter, and this would help to explain the range of values usually quoted for polymers.[87] In view of the success of this work the solubility of polymers in other monomers, such as tetrahydrofuran and epoxides, could also produce interesting results. It is also possible to improve or increase the common solubility with the aid of added solvents so that other polymers and monomer could be used, as indicated below.

6:2 POLYSULPHONE-POLYCAPROLACTAM COPOLYMERS.

The experiments to determine the composition of the polysulphone-polycaprolactam copolymers shows them to be block copolymers in which the polysulphone units are, on average, only two or three units long.

The length of the polycaprolactam component for a particular copolymer depends on the polysulphone and catalyst concentrations. The physical properties of the copolymers indicate that they have useful properties but it would be desireable to prepare distinctive copolymers in which the size of the graft components can be varied.

Matzner[71] has shown that the molecular weight of the polysulphone components of the copolymers can be increased by the use of chlorine terminated polysulphones to initiate the polymerisation. The experiments were performed at 160°C and above with catalyst concentrations of 2 to 4 mole % and it is expected that the copolymers produced will contain some free polysulphone and polycaprolactam. If the experiments were to be performed at 150°C, with catalyst concentrations of the order of 1 to 2 mole % no polycaprolactam will be produced but a small amount of free polysulphone would be expected because of the reactivity of the ether link in the prepolymer at this temperature. By preparing chlorine terminated polysulphone polymers of varying molecular weight, and careful control of the reaction conditions it should be possible to prepare copolymers with varying compositions and a variety of properties.

This work has shown that compatible blends of polycaprolactam and polysulphone cannot be obtained by mechanical mixing in a Brabender Plastograph. Despite this it should be possible to blend either of the homopolymers with copolymers produced by techniques described in the present thesis and procude more compatible blends with desirable properties.

It might be easier, and more convenient, to do this in many cases rather than attempting to prepare copolymers with specific compositions.

As polysulphones have good heat resistant properties it might be expected that copolymers containing them could be used where homopolymers , such as nylon 6, could not. Copolymers could be formulated which would be less expensive than pure polysulphone but still have an excellent balance of physical properties. Increasing the molecular weight of the polysulphone components of the copolymers is expected to improve their thermal properties.

The physical properties of the copolymers indicate that they could be suitable for fibre forming. In order to determine this, fibres should be spun from the various copolymers which would show those which formed good fibres. The results would indicate the copolymer composition needed in order to produce fibres with the best physical properties.

It would be interesting to prepare polymers by dissolving both polysulphone and polycaprolactam in caprolactam and then to polymerise the monomer in the usual way. Phase inversion could be made to occur before polymerisation and as a result copolymer formation could only take place on the surface.

Because of the limited solubility of polymers the logical progression is to extend the system to include solvents. The use of solvents should reduce the reaction temperature, increase solubility and also increase the number of polymers and monomers which can be studied together.

An example where a solvent has been used successfully is the polymerisation of laurolactam in the presence of ethylene-ethyl acrylate copolymers using dioxan as the solvent.

6:3 POLYMER BLENDS WITH POLYCAPROLACTAM.

The physical properties of the blends prepared in this work showed that they had balances of properties inferior to those of the lactam homopolymer due to the incompatibility of the components. Although attempts to prepare blends with polycaprolactam by polymerising the monomer in the presence of a dissolved amorphous polymer were unsuccessful in yielding products with advantageous properties, some success might be achieved if the dissolved polymer were crystalline and compatible. Compatible blends were obtained when caprolactam was polymerised in the presence of other nylon homopolymers. The range of such homopolymers might be extended.

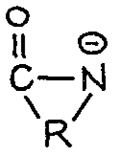
APPENDIX 1.

THE ANIONIC POLYMERISATION OF CAPROLACTAM.

The anionic polymerisation of caprolactam, first investigated with alkali metals and their hydrides as catalysts[66, 116-119] has been found to display a characteristic induction period,[120] indicating that certain active groups must be formed before polymerisation can begin. It has also been found that the introduction of molecules containing imide groups to the polymerisation mixture removed this induction period and accelerated the polymerisation.

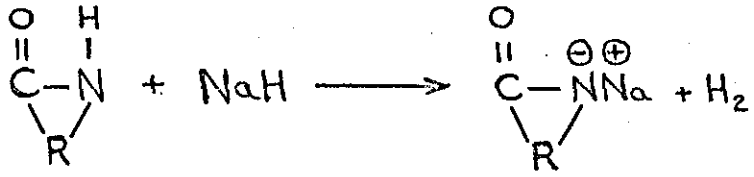
Following the finding of the cocatalytic influence of imide groups a mechanism for the polymerisation of lactams has been proposed.[121-123] Although caprolactam is the most studied member of the series, other lactams have been polymerised with degrees of success dependent upon the lactam ring size. The polymerisation mechanism is considered to be similar for all the lactams.

The first step in the anionic polymerisation of lactams is the formation of a lactam anion.



$R = (CH_2)_5$

by the reaction of the lactam with a selected base (equation 21)



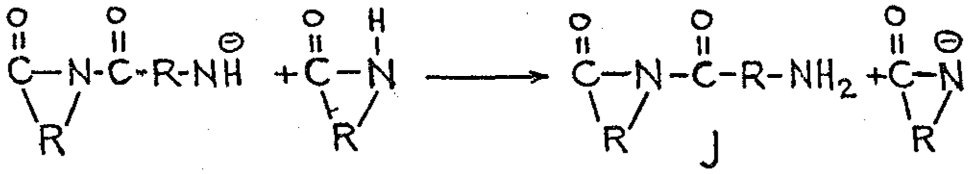
- - - - (21)

The types of bases used can be alkali metals, their azides, cyanides, hydrides, hydroxides, alkoxides or carbonates[66,116-119,122-126] aluminium alkyls[127,128] or Grignard compounds[118,129]

The lactam anion then reacts more slowly with a lactam molecule to form the very reactive anion H

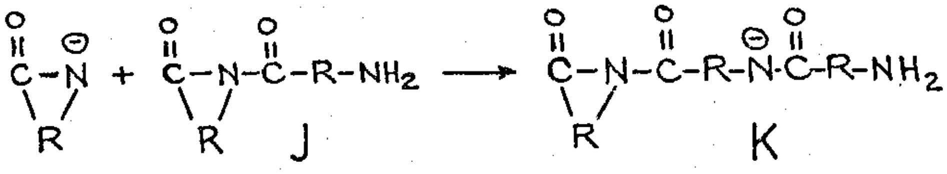
---- (27)

Once formed, anion H, being more basic than a lactam molecule, abstracts a hydrogen atom (from caprolactam) and reforms a lactam anion.



---- (28)

Polymerisation proceeds with transamidation by lactam anion (equation 29), followed by abstraction of a hydrogen atom (equation 30)



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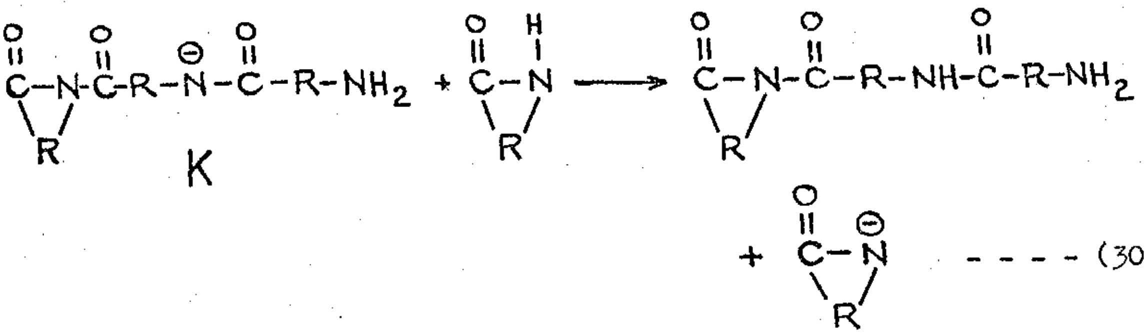
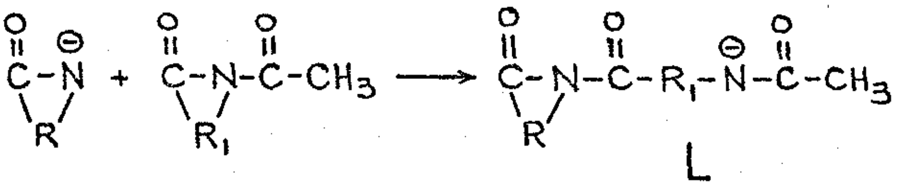


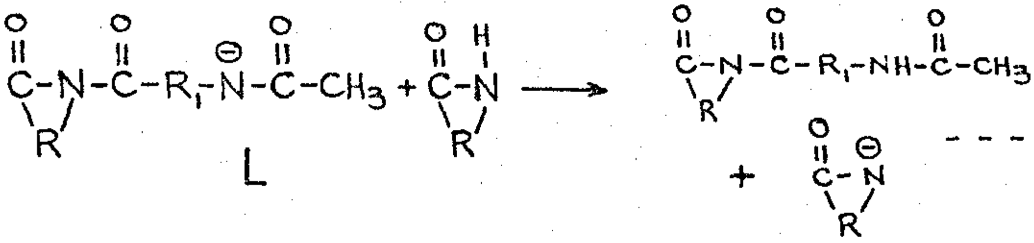
---- (30)

Anion K is more stable than anion H due to the presence of a carbonyl group delocalising and stabilising the negative charge. Consequently reaction 27proceeds more slowly than reaction 29. The long time for anion A formation is responsible for the induction period observed in lactam polymerisations without cocatalysts.[120] The imide dimer J has been isolted[130] and is suggested to be the actual initiating species necessary for the onset of propagation. The addition of compounds containing imide groups as cocatalysts to the polymerisation mixture removes the polymerisation rate dependence from reaction 27 to the more rapid transamidation reaction (equation 31). Here the imide type used is an N-acetyl lactam cocatalysts.



- - - - (31)

Polymerisation can then proceed by hydrogen atom abstraction.



- - - - (32)

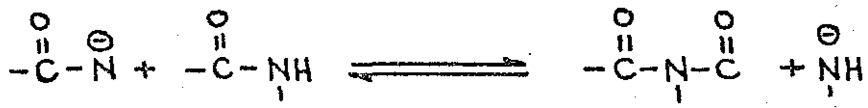
followed by further transamidation. The anion L is present for only a very short time and neutralisation occurs almost immediately following its formation.

In addition to the large number of bases (mentioned above) which can be used as polymerisation catalysts, many cocatalysts are reported, other than the N-acetyl lactam considered in equation 31.

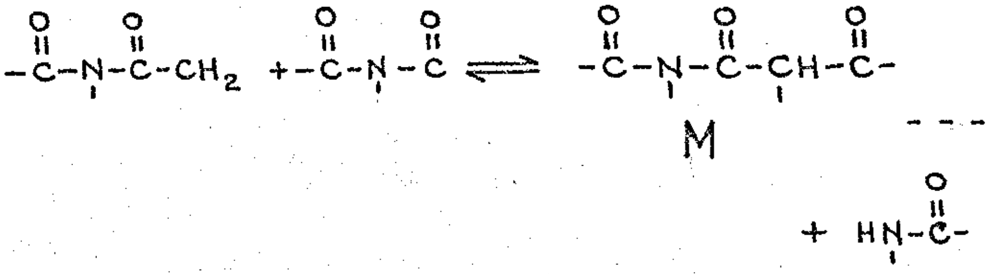
The main requirement of a cocatalyst is that the anion formed by the first addition of lactam should be stabilised so that polymerisation can proceed. This is achieved in anion L by the electro negative acetyl group delocalising the negative charge on the nitrogen atom. The cocatalysts reported in the literature include various N-acylated lactams[131-135] compounds reacting with lactams in situ to form N-acylated lactams (eg. acid chlorides, esters, anhydrides, isocyanates, ketones and carbonates[137-139]) phosphinyls, nitroso, sulphonyl and sulphide compounds[140] and many others. The most commonly used cocatalysts, however, are the N-acyl lactams because of their easy preparation, low cost and non-toxicity.

It is clear from the mechanism described above that the base catalysed polymerisation of lactams is quite different from other polymerisations in two respects. The first is that the propagating centre is not a radical but a cyclic amide link, and the second is that it is not a monomer molecule but a lactam anion which adds to the polymerisation chain. The lactam anion has been referred to as an activated monomer.[141] For such a polymerisation therefore, the concentrations of both the propagating species and lactam anion are determined by the concentration of base. Also,if the proton chain exchange equilibrium (equation 32) lies far to the right, the growth rate of each chain will be completely independent of the monomer concentration. In practice however, lactam polymerisations are found to be complex in the sense just described, and with respect to other details mentioned later.

In light of the mechanism described above, it is now possible to discuss the effects of increasing the catalyst concentration on the polymerisation of lactams. At low catalyst concentrations (up to about 0.6 mole %) few lactam anions are formed and fewer growing chains initiated due to degradation reactions by moisture and acidic compounds arising from imide groups.[68,141-144] These acidic groups have been identified as β keto acids and a suggested formation is given below.

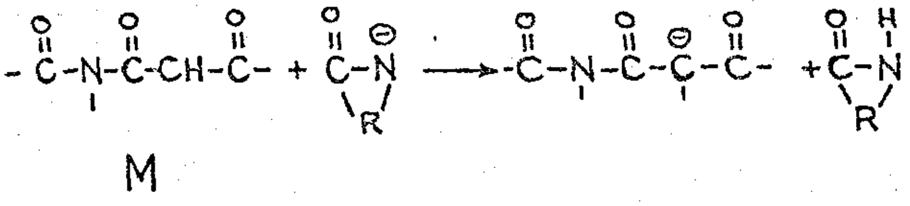


$$-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{N} + -\overset{\overset{O}{\|}}{C}-\underset{|}{N}H \rightleftharpoons -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-\overset{\overset{O}{\|}}{C} + \overset{\ominus}{\underset{|}{N}H} \quad ----(33)$$



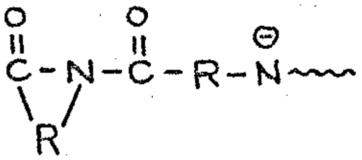
$$-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-\overset{\overset{O}{\|}}{C}-CH_2 + -\overset{\overset{O}{\|}}{C}-\underset{|}{N}-\overset{\overset{O}{\|}}{C} \rightleftharpoons \underbrace{-\overset{\overset{O}{\|}}{C}-\underset{|}{N}-\overset{\overset{O}{\|}}{C}-\underset{|}{C}H-\overset{\overset{O}{\|}}{C}-}_{M} + H\underset{|}{N}-\overset{\overset{O}{\|}}{C}- \quad ----(34)$$

Reaction 33, between an activated monomer or part of a linear chain, and another chain, gives an N-acyl amide, which, with a base catalysed condensation reaction (equation 34) results in an acylated alkylamide of a β keto acid M (called a keto imide). Keto imides are more acidic than the monomer and may consume lactam anions according to reaction 35.

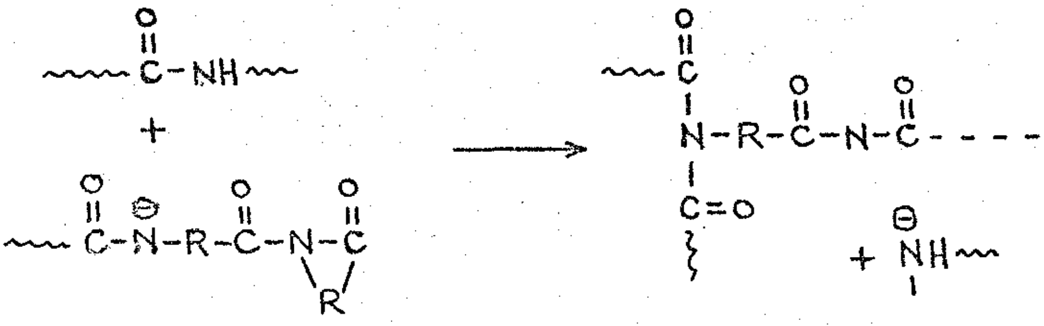


----(35)

At low catalyst concentrations therefore, lactam anion disappearance will have a large effect on the rate of polymerisation, With an excess of imide groups (cocatalyst) degradation reactions will destroy nearly all the lactam anions before polymerisation can occur, only a small amount of low molecular weight material being formed. As the catalyst concentration increases up to about 0.6 mole % the number of lactam anions formed is such that they will not all be consumed by imide degradation reactions and polymerisation can proceed. As the monomer is consumed the anion

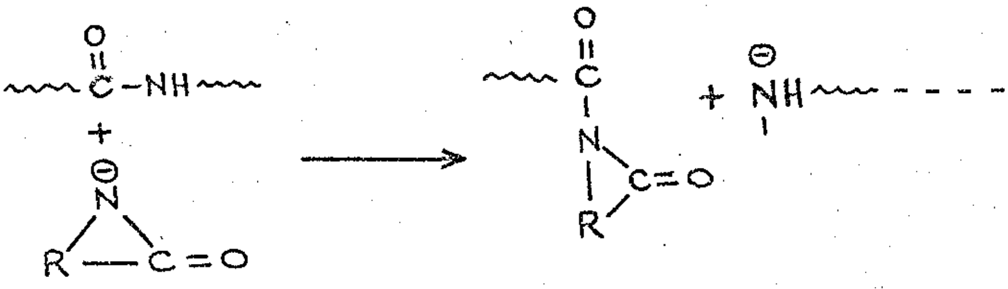


will be increasingly more difficult to deactivate as in the normal polymerisation reaction and chain degradation may be caused by rupturing the C-N bond in a polymer chain.



(36)

An alternative degradation reaction which has been proposed involves the lactam anion[145,146]

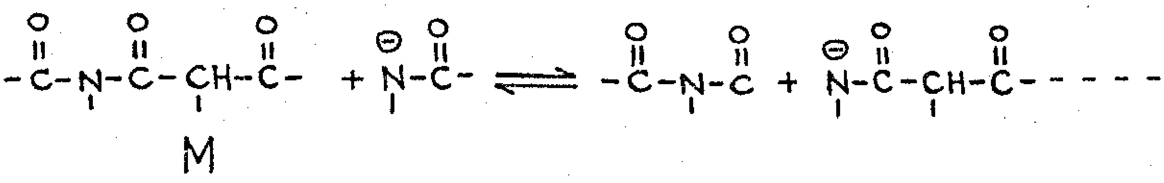


(37)

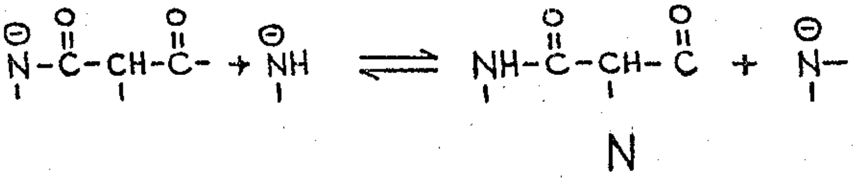
In both these reactions the length of the polymer chain will be decreased.

As the catalyst concentration is increased (0.8-1.8 mole %) more lactam anions are formed, more polymer chains are initiated and the mixture thickens more quickly due to faster monomer disappearance. Monomer consumption causes the yield to increase and reach 90% very quickly, but the chains become more restricted and the rate of monomer disappearance is greatly decreased above 90%. The greater number of lactam anions in the mixture at this stage means that degradation reactions such as 36 and 37 will occur.

When the catalyst concentration is increased even further (above about 2 mole %) even more lactam anions are formed. With these high catalyst concentrations however, the basicity of the medium increases and the dissociation of the lactam alt decreases[147] and this will probably decrease the rate of polymerisation. Slower polymerisation may also be caused by an increase in the number of degradation reactions because increasing the number of growing chains in the medium may result in greater numbers of non-polymerisation reaction at high conversions. The keto imide M may take part in trans-acylation reactions with amide anions (reaction 38) resulting in non-acylated alkylamides of β keto acids N, called keto amides (reaction 39).

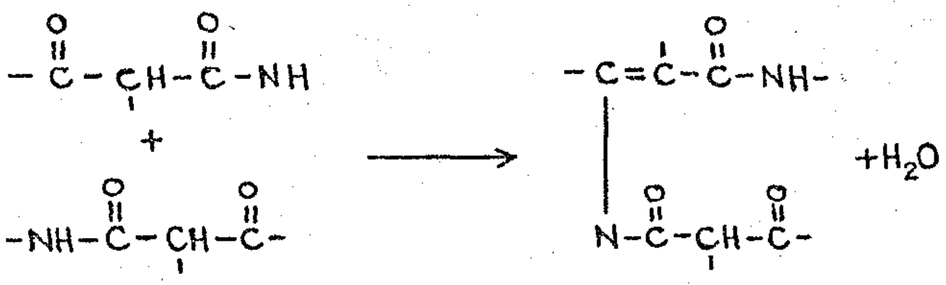


$$-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-\overset{O}{\overset{\|}{C}}-\underset{\substack{|\\M}}{CH}-\overset{O}{\overset{\|}{C}}- \;+\; \overset{\ominus}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}- \;\rightleftharpoons\; -\overset{O}{\overset{\|}{C}}-\underset{|}{N}-\overset{O}{\overset{\|}{C}} \;+\; \overset{\ominus}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{|}{CH}-\overset{O}{\overset{\|}{C}}- \quad (38)$$



$$\overset{\ominus}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{|}{CH}-\overset{O}{\overset{\|}{C}}- \;+\; \overset{\ominus}{\underset{|}{NH}} \;\rightleftharpoons\; \underset{|}{NH}-\overset{O}{\overset{\|}{C}}-\underset{\substack{|\\N}}{CH}-\overset{O}{\overset{\|}{C}} \;+\; \overset{\ominus}{\underset{|}{N}}- \quad (39)$$

These keto amides can undergo base catalysed condensation reactions which produce water.



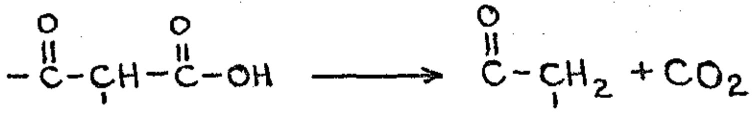
---- (40)

The water produced may then hydrolyse the ketoamides or imides to acids

$$-\overset{\overset{O}{\|}}{C}-\underset{|}{CH}-\overset{\overset{O}{\|}}{C}-NH- + H_2O \longrightarrow -\overset{\overset{O}{\|}}{C}-\underset{|}{CH}-\overset{\overset{O}{\|}}{C}-OH + NH_2-$$

---- (41)

β keto acids are unstable and decompose to ketones by liberating carbon dioxide.[148,149]



$$-\overset{\overset{O}{\|}}{C}-\underset{|}{CH}-\overset{\overset{O}{\|}}{C}-OH \longrightarrow \overset{\overset{O}{\|}}{C}-\underset{|}{CH_2} + CO_2$$

---- (42)

The water and carbon dioxide, in the presence of excess base, can form sodium carbonate which has been found during the polymerisation of polycaprolactam at high catalyst concentrations.[143] The amount found increases with increasing catalyst concentrations and this consumes more and more catalyst. The degradation reactions 36 and 37 will decrease with a decrease in the catalyst concentration. Polymer degradation reactions may also increase as the basicity increases because the dissociation of catalyst is decreased.

APPENDIX II.

POLYCAPROLACTAM-POLYSULPHONE COPOLYMERS PREPARED.

TABLE 1.

E SERIES No.	POLYSULPHONE CONCENTRATION (% BY WEIGHT)	CATALYST CONCENTRATION (MOLE %)	% POLYSULPHONE IN FINAL POLYMER	TEST.
E1	5.0	1.01	4.99	CONVERSIONS ETC.
E2	5.0	0.98	5.02	IMPACT
E3	5.0	1.04	5.02	TENSILE
E4	5.0	1.00	5.01	TENSILE
E5	5.0	0.96	5.01	TENSILE
E6	5.0	0.95	4.97	IMPACT
E7	5.0	0.98	4.98	IMPACT
E8	5.0	0.98	5.02	CONVERSIONS ETC.
E9	5.0	1.02	5.00	TENSILE
E10	5.0	0.98	4.99	IMPACT
E11	5.0	0.98	5.00	IMPACT
E12	5.0	0.97	5.03	IMPACT
E13	5.0	1.03	5.0	IMPACT

TABLE 2.

F SERIES No.	POLYSULPHONE CONCENTRATION (% BY WEIGHT)	CATALYST CONCENTRATION (MOLE %)	% POLYSULPHONE IN FINAL POLYMER	TEST
F1	10.0	1.01	10.01	TENSILE
F2	10.0	0.96	9.95	TENSILE
F3	10.0	1.04	10.00	IMPACT
F4	10.0	1.01	10.02	IMPACT
F5	10.0	0.99	10.01	IMPACT
F6	10.0	1.00	9.97	IMPACT
F7	10.0	1.05	10.00	IMPACT
F8	10.0	0.99	10.02	IMPACT
F9	10.0	1.02	9.99	IMPACT
F10	10.0	0.97	10.00	CONVERSIONS ETC.
F11	10.0	0.99	10.02	TENSILE
F12	10.0	0.97	10.02	TENSILE
F13	10.0	0.97	9.99	CONVERSIONS ETC.

TABLE 3.

G SERIES No.	POLYSULPHONE CONCENTRATION (% BY WEIGHT)	CATALYST CONCENTRATION (MOLE %)	% POLYSULPHONE IN FINAL POLYMER	TEST
G1	15.0	1.01	14.99	IMPACT
G2	15.0	1.00	14.93	CONVERSIONS ETC
G3	15.0	0.97	15.00	TENSILE
G4	15.0	1.01	14.96	TENSILE
G5	15.0	0.98	15.02	TENSILE
G6	15.0	0.96	15.01	IMPACT
G7	15.0	1.03	15.02	IMPACT
G8	15.0	1.00	15.08	TENSILE
G9	15.0	1.01	15.00	CONVERSIONS ETC.
G10	15.0	0.99	15.00	IMPACT
G11	15.0	0.99	15.03	IMPACT
G12	15.0	0.99	15.02	IMPACT.

TABLE 4

H SERIES No.	POLYSULPHONE CONCENTRATION (% BY WEIGHT)	CATALYST CONCENTRATION (MOLE %)	% POLYSULPHONE IN FINAL POLYMER	TEST
H1	5.0	2.01	4.99	IMPACT
H2	5.0	1.98	4.99	IMPACT
H3	5.0	2.00	5.00	TENSILE
H4	5.0	1.97	4.97	TENSILE
H5	5.0	1.98	5.00	IMPACT
H6	5.0	1.95	4.98	TENSILE
H7	5.0	2.00	5.03	CONVERSIONS ETC
H8	5.0	1.98	5.00	IMPACT
H9	5.0	1.97	4.99	IMPACT
H10	5.0	2.00	4.98	TENSILE
H11	5.0	1.99	4.98	IMPACT
H12	5.0	2.01	4.99	CONVERSIONS ETC.
H13	5.0	1.98	4.99	IMPACT.

TABLE 5.

J SERIES No.	POLYSULPHONE CONCENTRATION (% BY WEIGHT)	CATALYST CONCENTRATION (MOLE %)	% POLYSULPHONE IN FINAL POLYMER	TEST
J1	10.0	1.98	9.98	TENSILE
J2	10.0	2.03	10.01	IMPACT
J3	10.0	1.99	9.99	IMPACT
J4	10.0	2.01	10.00	IMPACT
J5	10.0	2.05	10.04	TENSILE
J6	10.0	1.96	9.97	TENSILE
J7	10.0	2.03	9.99	IMPACT
J8	10.0	1.99	10.02	CONVERSIONS ETC.
J9	10.0	1.98	9.99	CONVERSIONS ETC.
J10	10.0	2.02	10.00	TENSILE
J11	10.0	2.01	10.00	IMPACT
J12	10.0	2.03	9.98	IMPACT

TABLE 6.

K SERIES No.	POLYSULPHONE CONCENTRATION (% BY WEIGHT)	CATALYST CONCENTRATION (MOLE %)	% POLYSULPHONE IN FINAL POLYMER	TEST
K1	10.0	0.99	9.99	CONVERSIONS ETC.
K2	10.0	1.01	10.02	CONVERSIONS ETC.
K3	10.0	1.02	10.04	TENSILE
K4	10.0	1.02	10.00	TENSILE
K5	10.0	0.97	10.01	TENSILE
K6	10.0	1.02	10.01	IMPACT
K7	10.0	0.98	10.03	IMPACT
K8	10.0	1.00	10.01	TENSILE
K9	10.0	1.03	9.99	IMPACT
K10	10.0	1.00	10.04	IMPACT
K11	10.0	1.00	10.02	IMPACT
K12	10.0	0.99	10.02	IMPACT.

APPENDIX III.

TABLE.1.

POLYCAPROLACTAM HOMOPOLYMERS PREPARED.

SERIES NO.	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE %)	TEST
N1	1.02	0.10	CONVERSIONS
N2	1.01	0.11	IMPACT
N3	0.99	0.11	IMPACT
N4	1.03	0.11	IMPACT
N5	0.98	0.10	TENSILE
N6	0.98	0.11	TENSILE
N7	1.01	0.10	TENSILE
N8	1.00	0.11	IMPACT
P1	2.04	0.11	CONVERSIONS
P2	1.98	0.11	IMPACT
P3	1.98	0.11	IMPACT
P4	1.98	0.11	TENSILE
P5	2.01	0.11	IMPACT
P6	1.99	0.11	IMPACT
P7	2.01	0.11	TENSILE
Q1	1.02	0.21	TENSILE
Q2	1.02	0.21	IMPACT
Q3	1.00	0.21	CONVERSIONS
Q4	0.98	0.21	TENSILE
Q5	0.99	0.21	IMPACT
Q6	1.02	0.21	IMPACT
Q7	0.98	0.21	IMPACT
R1	1.99	0.21	TENSILE
R2	2.03	0.21	IMPACT
R3	2.01	0.21	TENSILE
R4	2.03	0.21	IMPACT
R5	1.98	0.21	CONVERSIONS
R6	1.99	0.21	IMPACT
R7	2.02	0.21	IMPACT

TABLE 2.

POLYCAPROLACTAM-POLYSTYRENE POLYMER BLENDS PREPARED.

SERIES NO.	% POLYSTYRENE IN FINAL POLYMER	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE %)	TEST
S1	4.98	1.00	0.11	TENSILE
S2	4.96	0.97	0.11	IMPACT
S3	4.99	0.99	0.11	IMPACT
S4	4.99	1.00	0.11	CONVERSION
S5	5.00	0.99	0.11	IMPACT
S6	5.00	1.01	0.11	IMPACT
T1	4.95	1.97	0.22	CONVERSION
T2	4.96	1.98	0.22	TENSILE
T3	4.97	2.00	0.22	IMPACT
T4	4.99	1.98	0.22	IMPACT
T5	4.97	1.95	0.22	IMPACT
T6	4.96	2.00	0.22	IMPACT
U1	9.98	2.03	0.23	IMPACT
U2	9.96	1.99	0.23	IMPACT
U3	9.96	2.02	0.23	TENSILE
U4	9.95	2.00	0.23	TENSILE
U5	9.95	2.01	0.23	CONVERSION
V1	15.07	2.02	0.25	TENSILE
V2	14.95	1.98	0.25	IMPACT
V3	15.04	2.04	0.25	CONVERSION
V4	15.08	2.05	0.26	IMPACT.

TABLE 3.

POLYCAPROLACTAM - IMPACT STYRENE POLYMER BLENDS PREPARED.

SERIES NO.	%IMPACT STYRENE IN FINAL POLYMER	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE %)	TEST
W1	5.00	1.02	0.11	TENSILE
W2	5.01	0.96	0.11	IMPACT
W3	5.01	1.00	0.11	CONVERSION
W4	4.97	0.99	0.11	IMPACT
W5	5.00	0.99	0.11	IMPACT
W6	4.96	1.00	0.11	IMPACT
X1	5.01	2.01	0.22	TENSILE
X2	5.02	2.01	0.22	CONVERSION
X3	5.02	2.02	0.22	IMPACT
X4	5.05	2.02	0.22	IMPACT
X5	5.05	2.03	0.22	IMPACT
X6	5.02	2.01	0.22	IMPACT
Y1	10.03	1.99	0.24	TENSILE
Y2	10.05	1.98	0.24	IMPACT
Y3	10.02	2.00	0.24	IMPACT
Y4	10.04	2.02	0.24	TENSILE
Y5	10.01	1.99	0.24	IMPACT
Y6	10.01	2.00	0.24	IMPACT
Y7	10.00	1.99	0.24	CONVERSION
Z1	15.01	2.00	0.25	IMPACT
Z2	14.96	1.98	0.25	IMPACT
Z3	14.92	1.98	0.25	TENSILE
Z4	14.99	1.99	0.25	TENSILE
Z5	14.95	2.03	0.25	CONVERSION

TABLE 4.

S.B.S. THERMOPLASTIC RUBBER - POLYCAPROLACTAM POLYMER BLENDS PREPARED.

SERIES NO.	%THERMOPLASTIC RUBBER IN FINAL POLYMER	CATALYST CONCENTRATION (MOLE %)	COCATALYST CONCENTRATION (MOLE%)	TEST
AA1	5.08	2.02	0.23	IMPACT
AA2	5.02	1.99	0.23	IMPACT
AA3	5.05	2.00	0.23	TENSILE
AA4	5.09	2.02	0.23	TENSILE
AA5	5.10	2.05	0.23	CONVERSION
BB1	10.10	2.04	0.24	CONVERSION
BB2	10.06	2.05	0.24	IMPACT
BB3	10.06	1.98	0.24	IMPACT
BB4	9.96	2.00	0.24	TENSILE
BB5	10.01	2.03	0.24	TENSILE
CC1	15.09	2.05	0.26	TENSILE
CC2	15.05	2.02	0.26	IMPACT
CC3	15.03	2.06	0.26	IMPACT
CC4	14.96	2.00	0.26	CONVERSION

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