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BLOCK COPOLYMERS

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I. INTRODUCTION

Until recently, the properties of polymeric materials were varied chiefly by altering the chemical composition and structure of the original monomers, the mean molecular weight of the polymer, the cross-linking of the polymer chain, the molecular-weight distribution, etc. Various methods for modifying macromolecular compounds are now becoming increasingly important. We think that one of the most promising methods, as far as industry is concerned, for modifying polymeric materials involves block and graft copolymerisation.

Block copolymers are macromolecular compounds whose main chain consists of two or more polymer blocks with different chemical composition or spatial configuration, joined to one another either directly or by means of low-molecular bifunctional compounds. The properties of block copolymers are generally determined by the properties of the individual homopolymeric sections in the main chain, but block copolymers also exhibit a number of properties which are not shown by the polymer fragments composing the main chain. An example is the block copolymer, of the diphilic type, consisting of blocks of aliphatic polyester and poly(methacrylic acid). This block copolymer, unlike poly(methacrylic acid), can be melted and is soluble in a mixture of acetone and alcohol, but is insoluble in water. The possibility of using familiar monomers to prepare polymeric materials exhibiting new properties fundamentally different from those of the corresponding homopolymers has led to the recent publication of a large number of papers and reviews [1-29] dealing with the synthesis and study of block copolymers. A classification of block copolymers has now become necessary. We suggest that the most rational basis for a classification of block copolymers is provided by the structural-chemical principle proposed by Korshak[30] for macromolecular compounds. This principle makes it possible to show directly in the name of the block copolymer the chemical character and structural features of its component blocks, their interconnection, and also the position occupied by the given block copolymer in a series of other macromolecular compounds. By analogy with the previously-proposed classification for graft copolymers[31,32], we propose a classification according to which block copolymers can be divided into three types:

1. Homochain block copolymers (main chain consisting of polymeric homochain blocks).
2. Heterochain block copolymers (main chain consisting of polymeric heterochain blocks).
3. Homo-heterochain block copolymers (main chain consisting of polymeric homochain and heterochain blocks).

In the synthesis of block copolymers, the polymer fragments of the main chain may form either highly-ordered (crystalline) or disordered (amorphous) regions in the structure of the block copolymer. To reflect these structural features of block copolymers, the above types of block copolymer can in turn be subdivided into the following three groups: (a) amorphous block copolymers (all polymer fragments of the main chain amorphous); (b) crystalline block copolymers (all polymer fragments of the main chain crystalline); and (c) crystalline-amorphous block copolymers (polymer fragments of the main chain having structures with different degrees of order).

The classification of a block copolymer in a given type and group is independent of whether the polymer blocks making up the block copolymer are joined to one another directly or by means of bifunctional low-molecular compounds.

The proposed classification covers all possible types of block copolymer, including block copolymers consisting of organic and inorganic polymer fragments, natural and synthetic block copolymers, and also the so-called stereo-block copolymers and optically active block copolymers.

Block copolymers are prepared by mechanochemical, radiochemical, and other chemical methods. The first two methods give not only block copolymers but also graft copolymers, and the final product is a mechanical mixture of homopolymers with block and graft copolymers. The separation of this mixture is not always possible. It is

not the aim of the present review to examine in detail the synthesis of block copolymers by all known methods, and we shall restrict ourselves to chemical methods of synthesis.

II. HOMOCHAIN (CARBOCHAIN) BLOCK COPOLYMERS

The greatest number of papers has been devoted to block copolymers of this type, evidently because of the possibility of synthesising carbochain block copolymers by the usual methods for the homopolymerisation of vinyl monomers. All the methods described for the preparation of carbochain block copolymers are variants of vinyl monomer polymerisation, taking place by a free-radical or ionic mechanism. Irrespective of the nature of the original materials, the block copolymers obtained by the first mechanism are generally amorphous copolymers, whereas those obtained by the second mechanism are crystalline or crystalline-amorphous block copolymers.

1. Synthesis of Block Copolymers by Radical Polymerisation

This method has found the widest application in the synthesis of carbochain block copolymers. Since there are many methods for preparing macroradicals capable of initiating carbochain block copolymerisation, this method is extending considerably the range of utilisation of polymerisation for the synthesis of polymers. The production of polymeric radicals and subsequent block copolymerisation can be carried out by a mechanochemical method involving the application of mechanical stress to the polymer chains by means of ultrasonic vibrations[33-36], rolling[37-43], vibration milling[44,45], the electrohydraulic effect[46,47], etc.[48-58] in the presence of a given monomer. Carbochain block copolymers can also be obtained by the action of various forms of high-energy ionising radiation on a polymer chain in the presence of the corresponding monomer[59-68]. The synthesis of carbochain block copolymers by chemical means can be achieved by the addition of "live" macroradicals to the monomer, by the initiation of the block copolymerisation reaction by macroradicals which retain their activity, or by macroradicals formed as a result of the decomposition of peroxide groups in the main chain of the homopolymer. The most complete studies have been made of the method for the synthesis of block copolymers based on the introduction, into the homopolymer block, of terminal groups which, depending on their chemical character, are capable of forming macroradicals and initiating subsequent block copolymerisation.

A. Methods based on the presence, in the polymer block, of active terminal groups capable of forming macroradicals initiating the polymerisation of monomers with the formation of block copolymers.

In this method, as in all other methods for the preparation of block copolymers, particular attention is paid, in the synthesis of the block copolymers, to the maximum or complete elimination of the simultaneous formation of graft copolymers and homopolymers. This task is complicated by the fact that the probability of side reactions leading to the formation of undesirable products is much greater under the conditions of synthesis of block copolymers than in homopolymerisation, since the process takes place in two stages.

Depending on the chemical character of the active terminal group introduced into the homopolymer block, the mechanisms of the formation of macroinitiators and the direct formation of block copolymers differ considerably, and it is impossible to give a general scheme for the preparation of block copolymers by this method.

Block copolymerisation initiated by terminal hydroperoxide groups. Homopolymer fragments containing terminal hydroperoxide groups are obtained by polymerising monomers in the presence of dihydroperoxides under conditions ensuring the homolytic decomposition of only one hydroperoxide group, to avoid the formation of an inactive homopolymer[69]. Some patents recommend for this purpose the use of polyfunctional hydroperoxides containing two or more hydroperoxide groups with different reactivities[70]; it is believed that this reduces the formation of homopolymer to a minimum. Most frequently, however, the dihydroperoxides of *p*- and *m*-diisopropylbenzene are used to obtain the polymeric hydroperoxide. To avoid initiation of the homopolymerisation of the primary monomer by the hydroxyl radical, the reaction is carried out in the presence of Fe^{2+} ions[71-73]. It has been suggested[74] that the formation of homopolymer blocks with terminal hydroperoxide groups should be regarded as a series of competing reactions whose kinetics can be examined by the method of Frost and Schwemer[75] with the condition that $[Fe^{2+}]_0 = 2[HOOROOH]_0$.

On the basis of the proposed mechanism for the reaction of the dihydroperoxide, monomer, and Fe^{2+}, it was found theoretically that the ratio

$$\frac{\text{Fe}^{2+}\text{ consumed as a result of oxidation by radicals}}{\text{monomer consumed as a result of initiation of polymerisation}} = \frac{[Fe^{2+}]}{[\bar{M}]}\left\{\frac{K_{10}[HOORO^{\cdot}] + K_{20}[\cdot OROM_n^{\cdot}] + K_{30}[\cdot ORO^{-}]}{K_{1i}[HOORO^{\cdot}] + K_{2i}[\cdot OROM_n^{\cdot}] + K_{3i}[\cdot ORO^{-}]}\right\}.$$

An analogous relationship in the form

$$\frac{\Delta Fe^{2+}_{total}\,\Delta^{*}Fe^{2+}}{2\Delta^{*}Fe^{2+} - \Delta Fe^{2+}_{total}} \quad \text{or} \quad \frac{\frac{1}{\Delta Fe^{2+}_{total}}}{\Delta Fe^{2+}_{total} - \Delta^{*}Fe^{2+}} - 2$$

can also be found experimentally, with the condition that the total quantity of Fe^{2+} used up in the course of the reaction (ΔFe^{2+}_{total}), and the proportion which has reacted with the hydroperoxide ($\Delta^{*}Fe^{2+}$) are known. $[Fe^{2+}]$ is calculated from the experimental data and $[\bar{M}]$ is taken as equal to the concentration of the polymerising monomer.

In the second stage of the synthesis — the synthesis of the actual block copolymer — an effort is made to carry out the reaction under conditions ensuring the minimum possibility of chain-transfer reactions[76]. The method described for the preparation of block copolymers was studied in detail by Molyneux[77] for the case of the block copolymer of styrene with methyl methacrylate. In the first stage of the synthesis, thermal polymerisation of styrene was carried out at 70° in the presence of a dihydroperoxide *m*-diisopropylbenzene to give polystyrene with terminal hydroperoxide groups.

The block copolymer was prepared by suspension polymerisation at 0–25° in the presence of Fe^{2+} ions and sodium pyrophosphate. The reaction products contain polymethyl methacrylate blocks in numbers either equal to or double

the number of original polystyrene blocks. Turbidimetric titration with subsequent extraction showed that the concentration of block copolymers in these products is ~ 10%. This low yield of block copolymers is due to the absence of terminal hydroperoxide groups from a considerable proportion of the polystyrene blocks (~ 25%) and to homopolymerisation of methyl methacrylate. It is assumed that the latter is due to chain transfer to benzene from polymeric radicals, which are localised in the droplets and have a long life time, and also to the reaction of monomer with radicals formed in the organic or aqueous phases of the suspension as a result of the decomposition of hydroperoxide remaining in the polystyrene. The marked non-uniformity of the block copolymer composition (a mixture of block copolymers of two types A_nB_m and $B_mA_nB_m$ is formed) is apparently due to the fact that the original hydroperoxide derivatives of polystyrene contain either one or two hydroperoxide groups.

The chain-transfer reaction can also be used to obtain a homopolymer block with a terminal hydroperoxide group. It has been reported[78] that polymers or statistical copolymers of alkenes, containing terminal hydroperoxide groups, are obtained by polymerising alkenes or their mixtures at 0–35° in an aqueous emulsion containing 0.05–20 wt.% of monomer, in the presence of diisopropylphenyl dihydroperoxide as initiator and a chain-terminating reagent. The polymeric derivatives formed in this way are isolated and used as initiators for block copolymerisation with vinyl monomers. It is recommended that these polymers be stored at a temperature not exceeding 30°, to avoid decomposition of the terminal hydroperoxide groups.

Block copolymerisation initiated by terminal peroxide groups. Terminal peroxide groups are introduced into homopolymer fragments using phthaloyl peroxide[79]. Smets[80] showed that if styrene is kept for 5–6 h at 75° in the presence of 0.5% phthaloyl peroxide, polystyrene containing terminal peroxide groups is formed. This polymeric peroxide, dissolved in a benzene solution of methyl methacrylate, initiates a block copolymerisation reaction at 100°; after treatment for 5 h, the quantity of methyl methacrylate converted amounts to 40%. More detailed study of polymeric derivatives of phthaloyl peroxide[81,82] showed that to obtain a block copolymer in good yield it is necessary to take account of the relative reactivity and ability to undergo chain-transfer reactions shown by the monomeric components taking part in the block copolymer formation. For example, polystyrene containing terminal phthaloyl peroxide groups readily initiates the polymerisation of methyl methacrylate and ethyl α-chloroacrylate at 100° but does not initiate the polymerisation of vinyl acetate or vinylpyrrolidone, whereas the analogous peroxide derivative of poly(vinyl acetate) readily initiates the polymerisation of styrene and ethyl α-chloroacrylate under the same conditions. The solubility of the block copolymers obtained in this way differed significantly from that of the corresponding homopolymers, and this made it possible to isolate them in pure form. Analysis of the infrared spectra of the block copolymer of styrene with methyl methacrylate showed that the concentration of styrene units in the block copolymer varies from 22% to 30%.

Another method for introducing terminal peroxide groups into homopolymer blocks involves the polymerisation of styrene in the presence of t-butyl hydroperoxide and Cu^{2+} ions[83,84]. The decomposition of t-butyl hydroperoxide in the presence of Cu^{2+} ions evidently leads to the formation of $(CH_3)_3COO^{\cdot}$ and $(CH_3)_3CO^{\cdot}$ radicals, the first of which, probably as a result of recombination with the growing polystyrene macroradical, form active terminal peroxide groups capable of initiating subsequent block copolymerisation.

$$(CH_3)_3COO^{\cdot}+\dot{C}H(C_6H_5)CH_2CH(C_6H_5)CH_2 - \cdots \longrightarrow$$

$$\longrightarrow (CH_3)_3COOCH(C_6H_5)CH_2-CH(C_6H_5)CH_2 - \cdots .$$

An interesting property of this polymeric peroxide is its relatively high thermal stability; it does not decompose below 60°, even when exposed to ultraviolet light.

Study of the kinetics of formation of these macroperoxides[85,86] showed that the order of the reaction involved in the initiation of the primary monomers by t-butoxy- and t-butylperoxy-radicals decreases with increase in their concentration, since the primary radicals take part in a chain-termination reaction. In the block copolymerisation of these macroradicals with methyl methacrylate and vinyl acetate, it was observed that increase in the viscosity of the reaction medium decreased the yield of block copolymer.

The use of 2–8 mole % $(CH_3)_3COOOC(CH_2)_4COOOC(CH_3)_3$ has been recommended for the initiation of the polymerisation of the primary monomer in the synthesis of analogous polymeric peroxide derivatives[87]. The polymerisation is carried out homogeneously or heterogeneously at 70–90°. This method has been used to prepare homopolymer blocks of styrene, vinyl chloride, methyl methacrylate, and vinyl acetate, containing one terminal peroxide group. The absence of macromolecules containing no terminal peroxide groups is apparently due to the extremely low initiating power of the $(CH_3)_3CO^{\cdot}$ formed in the decomposition of the initiator

$$(CH_3)_3COOOC(CH_2)_4COOOC(CH_3)_3 \longrightarrow (CH_3)_3COOOC(CH_2)_4^{\cdot} + CO_2 + {}^{\cdot}OC(CH_3)_3.$$

Satisfactory results were obtained in the block copolymerisation of polystyrene with acrylonitrile, of poly(vinyl acetate) with styrene, and of poly(vinyl chloride) with styrene, although the block copolymers obtained had a low polymerisation coefficient. Block copolymers with vinyl chloride could not be obtained, because of the high rate constant of the chain-transfer reaction via the monomer.

Block copolymerisation initiated by terminal amino-groups. In the synthesis of carbochain block copolymers by chain-transfer reactions[88], the use of terminal amino-groups in homopolymer blocks as macromolecular chain-transfer reagent has been proposed[89]. The rate constants for chain transfer were determined for the radical polymerisation of styrene and vinyl acetate in the presence of primary, secondary, and tertiary amines[90]. The highest values of the rate constant for chain transfer were observed for the polymerisation of acrylonitrile and methyl methacrylate in the presence of triethylamine[91]; this is attributed to the formation of ionic structures in the transition state. Bamford and coworkers[92] showed that to obtain block copolymers of the type A_nB_m it is best to carry out the homopolymerisation of the monomer A in the presence of triethylamine; chain transfer takes place through the latter with the formation of a compound of the type

$$AA\cdots A-CH\begin{matrix}N(C_2H_5)_2\\ \\ CH_3\end{matrix}.$$

This polymeric product was used as macromolecular chain-transfer agent in the homopolymerisation of the monomer

under conditions ensuring a high degree of chain transfer by the growing radical.

To reduce the formation of homopolymer to a minimum, it is recommended that the second stage of the synthesis of the block copolymer be carried out using monomers for which the life time of the kinetic chain during polymerisation is appreciable. A series of equations for calculating kinetics of block copolymerisation were proposed for the case of the block copolymer of methyl methacrylate with acrylonitrile. In the derivation of the equation, which makes it possible to determine the number of transfer acts (n.t.) through each polymeric molecule formed, it was postulated that chain transfer takes place only through the polymer chain. The equation is

$$\text{n.t.} = (k_3'[S_A] + k_3''[E])\{k_3'[S_A] + k_3''[E] + (Ik_4)^{1/2}\}^{-1},$$

where $[S_A]$ is the concentration of poly(methyl methacrylate), $[E]$ the concentration of terminal groups, I the rate of initiation, k_3' and k_3'' the rate constants for the chain-transfer reaction through the elementary units of the polymer chain and through the terminal amino-groups respectively, and k_4 the mean rate constant for the chain-termination reaction resulting from disproportionation.

The weight-average concentration of poly(methyl methacrylate) fragments (m) is calculated from the equation

$$m = a(k_3'[S_A] + k_3''[E])\{k_3'[S_A] + k_3''[E] + (Ik_4)^{1/2}\}^{-1},$$

where a is the polymerisation coefficient for poly(methyl methacrylate) with terminal amino-groups.

The following equation was proposed for the number-average polymerisation coefficient of polyacrylonitrile $\bar{P}$ for a low degree of conversion

$$\bar{P} = k_2[B]\{k_3'[S_A] + k_3''[E] + (Ik_4)^{1/2}\}^{-1},$$

where k_2 is the rate constant for the reaction of chain growth and $[B]$ the acrylonitrile concentration.

Bamford and White [93] found that the dependence of the concentration of block copolymer molecules of the type A_nB_m, containing a units of monomer A and b units of monomer B, $[P_{ab}]$, on the quantities a and b is given by the equation

$$[P_{ab}] = [S_B]\alpha^{a-1}(1-\alpha)^2\beta^b(1-\beta)k_3'[S_A]/k_2[B],$$

where $[S_A]$ and $[S_B]$ are the concentrations of the homopolymer blocks A_n and B_m respectively, α and β the probability factors for growth of the homopolymer chains of monomers A and B, $[B]$ is the concentration of monomer B, and k_3' and k_2 are the rate constants for the reactions of chain transfer and chain growth respectively. These equations were used to find the block copolymer distribution with respect to chain length ($r = a + b$) for a given composition ($a/b = c$) and the distribution with respect to composition for a given chain length. It was shown that the quantity of graft copolymer formed as side product is $[k'/k''(1 - \alpha)]$ times the concentration of block copolymers, where k' and k'' are the rate constants for the reactions of chain transfer by any unit of the polymer chain and by the terminal amino-group of the polymer formed by the polymerisation of monomer A. From this it follows that with increase in the polymerisation coefficient of the original monomer, equal to $1/(1 - \alpha)$, the concentration of impurity increases, although this is also accompanied by the formation of a block copolymer with greater molecular weight. Since the block copolymer synthesised by means of terminal amino-groups is non-uniform with respect to composition and dimensions of the homopolymer fragments, it was considered advisable either to fractionate the macromolecular chain-transfer agent thoroughly before the synthesis of the actual block copolymer or to extract the low-molecular fractions from it with a suitable solvent.

A polymer containing a terminal aromatic amino-group is obtained by a polymerisation reaction initiated by a diazonium salt and an aromatic acid containing a free amino-group or a group from which a free aromatic amino-group can be prepared by subsequent reactions. This reaction was used to obtain an acrylonitrile homopolymer with a terminal amino-group, and after diazotisation this was used as macromolecular initiator for block copolymerisation with acrylonitrile and 2-methyl-5-vinylpyridine [94,95].

Block copolymerisation initiated by terminal groups containing halogen. Homopolymeric blocks with terminal halogen atoms absorb light with wavelength 2880–3500 Å, are raised to an excited state, and dissociate into free reactive polymeric radicals which are used as macromolecular initiators in block copolymerisation. The macromolecular halides are usually prepared by the thermal or photolytic polymerisation of styrene [96,97] or methyl methacrylate [98] in the presence of CBr_4 or $CBrCl_3$ which terminate the chain by a chain-transfer reaction.

In the second stage of the synthesis of the block copolymer, the macrohalide obtained is irradiated with ultraviolet light in the presence of a vinyl monomer, for example, methyl methacrylate, styrene, acrylonitrile, etc. The macroradical formed as a result of irradiation initiates the secondary polymerisation with the formation of the block copolymer, which can be isolated by fractionation on a column using the method developed by Baker and Williams [99].

The centres initiating block copolymerisation are formed only by decomposition of the C–Br group, since CCl_3 groups do not undergo photolytic decomposition under the conditions of the synthesis, whereas CBr_3 groups undergo further photolysis and are converted into centres initiating block copolymerisation. Chlorine-containing block copolymers are obtained in analogous fashion [100]. Hydrophilic block copolymers are obtained by polymerising acrylic acid in the presence of organic bromine-containing compounds with three or four carbon atoms and three bromine atoms. The resulting bromine-containing acrylic acid homopolymer is dissolved in an inert aqueous medium with another vinyl monomer, for example acrylamide, and the mixture is irradiated with ultraviolet light to give the block copolymer [101,102].

Block copolymerisation initiated by terminal groups containing sulphur. In the polymerisation of vinyl monomers in the presence of organic compounds containing sulphur atoms, it was found that the latter take part in chain-transfer reactions with the formation of homopolymeric blocks containing terminal SH groups [98,103]. These polymers are capable of undergoing photolytic decomposition at the terminal group, so that they may initiate block copolymerisation when irradiated with ultraviolet light in the presence of vinyl monomers. An analogous ability to undergo chain-transfer reactions is shown by various organic disulphides [104], and disulphides such as tetraethylthiuram disulphide† are used

† Bis(diethylthiocarbamoyl) disulphide (Ed. of Translation).

simultaneously to initiate the polymerisation of the primary monomer.

The polymerisation of styrene using tetraethylthiuram disulphide as initiator leads to the formation of polymer blocks with terminal sulphur-containing groups capable of undergoing photolysis with the formation of macroradicals which initiate block copolymerisation. A block copolymer of styrene with methyl methacrylate was prepared in this way [105]. Analysis showed that the product of this block copolymerisation consisted of 40% pure block copolymer, 30% styrene homopolymer, and 30% methyl methacrylate homopolymer [106]. Block copolymers of styrene with vinyl acetate were synthesised in analogous fashion in yields of more than 70%. [107] These block copolymers are soluble in most hydrocarbons and ketones, and are insoluble in methanol. The poly(vinyl acetate) block of this block copolymer can then be hydrolysed with a methanol solution of alkali to give the block copolymer of styrene with vinyl alcohol [108]. This block copolymer is insoluble in benzene, methanol, and water, and merely swells in these solvents; it is partly soluble in phenol and cresol. Another method of using sulphur-containing organic compounds in the synthesis of block copolymers involves the polymerisation of styrene (initiator diisopropylphenyl monohydroperoxide) in the presence of cumenethiol as chain-transfer agent. Chain transfer leads to the formation of polystyrene with molecular weight 28 000 (compared with 83 000 for control specimens of polystyrene), from which it is concluded that about 25% of the polystyrene blocks contain terminal isopropyl groups. These terminal groups are readily oxidised to hydroperoxide groups to give polystyrene blocks with terminal hydroperoxide groups which are capable, in the presence of Fe^{3+} ions, of initiating the block copolymerisation of polystyrene with various vinyl monomers [109].

Block copolymerisation initiated by terminal groups consisting of acid hydrazides. Acrylonitrile is capable of undergoing polymerisation in the presence of the redox system consisting of acid hydrazides and Fe^{3+} ions. The initial rate of polymerisation of acrylonitrile in 1 *N* acetic acid solution at 40° is almost linearly dependent on the concentration product $[\text{acid hydrazide}]^{1/2}[Fe^{3+}]^{1/2}$. The polymerisation of acrylonitrile can be initiated in analogous fashion by using, instead of the monomeric acid hydrazides, polymeric blocks containing acid hydrazides as terminal groups. This method has been used to prepare block copolymers of polyaminotriazole with polyacrolein, exhibiting a high affinity for acid dyes [110].

B. Methods based on the presence, in the main chain of the polymeric block, of active groups capable of forming macroradicals which initiate the polymerisation of monomers with the formation of block copolymers.

Block copolymerisation initiated by dye molecules present in the leuco-form in the main chain of the polymeric block. On the basis of spectroscopic data obtained by Oster's method [111] in studies of the products of the photopolymerisation of vinyl compounds, in the presence of dyes (eosin, safranine, Acridine Orange), reducing agents (ascorbic acid, thiourea), and oxygen, it has been established that the dye molecules are incorporated in the polymer molecule in the leuco-form. The photosensitising effect of the dyes present in the polymer molecule can be used for the initiation of block copolymerisation [112]. The irradiation, with visible light, of ω-*N*-(aminoeosin)-poly(methyl methacrylate) containing 1 eosin group for every 48 methyl methacrylate groups, in acetic acid in the presence of thiourea and acrylamide gave a block copolymer of methyl methacrylate and acrylamide, with a concentration of second monomer residues equal to 40%. A block copolymer of methyl methacrylate with styrene was obtained in analogous fashion but in higher yield (concentration of second monomer 79%); hydrolysis of this block copolymer showed that the homopolymer blocks are joined to one another by leuco-groups.

Block copolymerisation initiated by peroxide groups present in the main chain of the polymer block. Peroxides formed in the polymer during storage are capable of decomposing to form macroradicals which initiate block copolymerisation [113]. To obtain block copolymers using these polymeric peroxides, specimens of poly(methyl methacrylate), polystyrene, and poly(vinyl acetate) are kept in the vapours of styrene, acrylonitrile, vinylidene chloride, vinyl acetate, and methyl methacrylate [114]. Despite the heterogeneity of the process, which decreases considerably the rate of the block copolymerisation, analysis of the product showed an appreciable concentration of block copolymers. In the bulk copolymerisation of methyl methacrylate, styrene, and vinyl acetate in the presence of oxygen, peroxide bonds are formed in the main chain of the polymer [115]. If this polymeric peroxide is swollen in monomer and then heated, the macroradicals formed in the thermal decomposition of the peroxide groups begin to initiate polymerisation of the monomer adsorbed on the particles of polymeric peroxide, with the formation of a block copolymer.

Peroxide groups can also be introduced into the main chain of a polymer by a variety of chemical methods. For example, the partial dehydrochlorination of poly(vinyl chloride) gives a polymer with a main chain containing double bonds, ozonisation of which gives peroxide groups capable of initiating the block copolymerisation of vinyl monomers [116].

C. Methods based on the presence, in the main chain of the polymeric block, of side branches capable of undergoing photolytic degradation with the formation of macroradicals which initiate the polymerisation of monomers with the formation of block copolymers.

Block copolymerisation initiated by macroradicals formed by the photolytic degradation of keto-groups present in the polymer in the form of side branches. Irradiation of poly(vinyl methyl ketone) with ultraviolet light of wavelength 3130 Å leads to decomposition of the polymer by photolytic degradation according to a scheme analogous to that for the decomposition of monomeric aliphatic ketones under identical conditions [117-119]. The resulting macroradicals are capable of initiating the homopolymerisation and block or graft copolymerisation of monomers such as methyl methacrylate and vinyl acetate. As in the case of simple radical polymerisation, the rate of the block or graft copolymerisation depends on the concentration of keto-groups and is proportional to the square root of the intensity of irradiation.

D. Methods based on the introduction, into the monomer, of a mixture of polymer-homologues containing free active radicals capable of initiating the polymerisation of monomers with the formation of block copolymers.

Block copolymerisation initiated by radicals which have not lost their activity. In a study of the photopolymerisation of methyl methacrylate, Melville [120] observed that growth of the polymer chains continues after irradiation has stopped, and that this "growing polymer" may initiate the polymerisation of chloroprene without irradiation. Thomas [121] suggested that polymeric chains capable of growth may be preserved in a solid polymer. These macroradicals may initiate block copolymerisation when brought into contact with vinyl monomers. In the block polymerisation of acrylonitrile or acrylamide, the polymer formed is insoluble in the original monomer and is precipitated; this precipitate retains a large quantity of free macroradicals capable of further growth. With increase in temperature or the addition of solvents, the radicals occluded in the polymer are liberated due to the unwinding of the coiled polymer molecules, and may become centres for the initiation of the polymerisation of a second monomer [122]. The yield of block copolymers in this block copolymerisation is generally low — less than 5% in the case of poly(acrylonitrile) and less than 8% in the case of poly(acrylamide). This low yield of block copolymer is due to the incomplete liberation of the radicals during the block copolymerisation; this was confirmed by electron paramagnetic resonance studies. A block copolymer of methyl methacrylate with styrene was synthesised in analogous fashion [123].

The products of the emulsion polymerisation of styrene and methyl methacrylate, under the conditions of micro-gel formation, also contain radicals capable of initiating block copolymerisation. It has been established by electron microscopy [124] that the block copolymerisation is accompanied by an increase in the dimensions of the particles of the micro-gel; no new particles are formed. It is not clear whether the block copolymerisation centres are situated inside the micro-gel particles or on their surface. No homopolymer is formed under these conditions. These radicals can be used to prepare the block copolymer of vinyl acetate with methyl methacrylate [35]. For this purpose vinyl acetate is emulsion polymerised under the influence of γ-radiation; the macroradicals thus formed initiate the polymerisation of the second monomer.

Block copolymerisation initiated by long-lived macroradicals. In the suspension polymerisation of a water-insoluble monomer in the presence of an aqueous solution of another monomer, the macroradicals formed may diffuse through the phase boundary and initiate the polymerisation of the second monomer with the formation of a block copolymer. Block copolymers of methacrylic acid with styrene and vinyl acetate were prepared in this way [125-127]. Because of the complex mutual solubility of the monomers in one phase, however, the resulting block copolymer has an extremely indefinite composition and is formed in low yield. Block copolymers of *N*-vinylpyrrolidone with styrene [128] and vinyl chloride [129] are obtained in analogous fashion. A slightly different method was proposed for the preparation of block copolymers soluble in water and capable of being used as settling agents and filter aids [130]. One or several vinyl compounds forming water-soluble polymers (for example, acrylic or methacrylic acids or their salts or amides) are polymerised in aqueous solution and a further 0.5–30 wt.% of a vinyl monomer containing sulphonic or phosphoric acid residues in the molecule is added to polymerise with the still active primary monomer, which is not removed from the polymerisation medium.

Another example of block copolymerisation initiated by macroradicals with relatively long lifetime is the so-called "dynamic" method of block copolymer synthesis proposed by Hicks and Melville [131-134]. The essential features of the method are as follows. Monomer A, containing a photosensitiser, passes through a capillary, a small section of which is irradiated with a powerful quartz mercury lamp, into a reservoir containing monomer B. Decomposition of the sensitiser in the irradiated section produces free radicals (up to 10^{-4} mole) which react with the molecules of monomer A and form polymeric radicals of the type AA... A$^{\cdot}$. When they enter the reservoir containing monomer B, these radicals continue to grow, with the attachment of molecules of monomer B. The polymer molecules formed in this way have the structure ...AAABBB... or ...AAABBBBBAAA..., depending on the mechanism of the chain-termination reaction. Calculation shows that at an appropriate rate of flow of monomer A through the capillary, the main bulk of the free radicals formed during the irradiation are not deactivated in the time taken for the reaction mixture to pass through the capillary and enter the reservoir containing monomer B. The results of the theoretical calculations are confirmed by direct determination of the quantity of polymer formed only in the capillary and the quantity of polymer formed in the reservoir containing monomer B. This method has been used to synthesise block copolymers of butyl acrylate and acrylonitrile (monomers A) with styrene, using as sensitiser the dinitrile of azocyclohexanecarboxylic acid. The structure of the polymers obtained was studied by ultraviolet spectroscopy. Block copolymers of n-butyl acrylate with 2-vinylpyridine were synthesised in analogous fashion [135]; study of these block copolymers showed that their molecules consist of a poly(vinyl pyridine) block and a block of a statistical copolymer of both monomers used for the synthesis, situated between blocks consisting of units of the first monomer. This structure in the products obtained is due to the presence of both monomers in the second stage of the synthesis of the block copolymer.

E. Methods based on inter-chain exchange reactions during radical polymerisation, leading to the formation of block copolymers.

In the radical polymerisation of vinyl monomers to appreciable degree of conversion, secondary processes take place [136] involving reaction between the macroradicals formed. These reactions are of two types: (1) inter-chain exchange — a process of repeated degradation and recombination of macroradicals, and (2) the cross-linking of chain macromolecules without the formation of a gel. As a model system for the synthesis of a block copolymer, in which inter-chain reactions might take place in more or less "pure" form, use has been made of mixed solutions of polymers, in which thermal decomposition of the initiators — the sources of the primary free radicals — was carried out. The formation of block copolymers, confirmed by ultraviolet spectroscopy, was observed in mixed solutions

of polystyrene and polyisobutene in toluene in the presence of benzoyl peroxide and methylphenyltriazole. A method based on sedimentation in a density gradient was used for the quantitative analysis of the products obtained.

As mentioned above, the properties of block copolymers show not only the properties of their component homopolymers but also, as a rule, new properties differing sharply from those of the homopolymer. Some block copolymers exhibit properties which are so unique that the isolation of the pure block copolymers and the study of their properties is of considerable practical and theoretical interest. A number of reviews have been devoted to methods of studying block copolymers [137,138]. In our opinion, the most promising qualitative methods for the identification of block copolymers are nephelometric [139] and turbidimetric [140] titration. An apparatus has been described [141] for automatic turbidimetric titration, which makes it possible to determine the presence of a block copolymer in its mixtures with homopolymers.

The applicability of X-ray structural analysis to the study of block copolymers was confirmed for the block copolymer of methyl methacrylate with acrylonitrile [142]. The X-ray diffraction patterns for the block copolymers are similar to those for a mechanical mixture of the homopolymers, but there are certain differences in the scattering of X-rays by the block copolymers. The weight-average molecular weight of the block copolymers can be determined by light-scattering methods. The applicability of Stockmayer's equation

$$(I_0/k'c)_{c\to 0} = (dn/dc)_0^2\,\overline{M}\omega + 2b\,(dn/dc)_0\,\{M\Delta x\} + b^2\{M\,(\Delta x)^2\},$$

to the determination of the weight-average molecular weight of block copolymers from the values of the reduced intensity of the scattering of light in three different solvents has been studied experimentally for the block copolymer of styrene with methyl methacrylate. The parameters for the polydispersity of composition $M\Delta x$ and $M(\Delta x)^2$ show satisfactory agreement with one another when any three measurements in different solvents are chosen [143].

The thermodynamic equations for solutions of homopolymers have been used to calculate the Hildebrand solubility parameters for statistical, block, and graft copolymers $\delta_i = \sqrt{(\Lambda_i - RT)/V_i}$, where Λ_i is the molar heat of volatilisation and V_i the molar volume of the ith component of the mixture. Using the subscripts A and B to denote the values of δ for the corresponding homopolymers, and the subscript 0 for the solvent, and taking $(\delta_A - \delta_B) = p$ (with the condition that $\delta_A > \delta_B$), $|\delta_0 - \delta_A| = \Delta\delta_A$, RT = = 600 cal, and $V_0 = 100$ cm^3, the authors obtained the following condition for the solubility of the statistical copolymers:

$$\Delta\delta_A + p(1-\beta) \leqslant {}^1/_6, \qquad (1)$$

where the solubility parameter $\delta_p = \delta_A\beta + \delta_B(1-\beta)$. This result was obtained from an analysis of the systems by the Flory–Huggins method. The derivation of this equation was based on the fact that the entropy (S) of the statistical copolymer is the same as the entropy of the homopolymer with the same polymerisation coefficient, whereas the heat of mixing ΔH depends on the interaction of the solvent with the main units of A and B. In the case of the block copolymers, it is necessary, in the calculation of the entropy, to make allowance for the fact that the volumes of the statistical segments are different for the homopolymers A and B. In the calculation of ΔH for the block copolymers, in the case of comparable homopolymers, the solubility condition is described by Eqn. (1), whereas for non-comparable homopolymers the solubility condition is described by the quadratic relation $(\Delta\delta_A)^2 - 2p(1-\beta)\Delta\delta_A + p^2(1-\beta) \leqslant (2^{-1} - z^{-1})RT/V_0$, where z is the coordination number of the Flory–Huggins quasi-lattice and β the volume fraction of monomer A in the statistical copolymer [144].

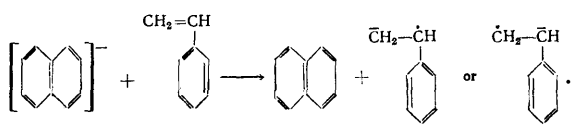
In the study of solutions of block copolymers of styrene with methyl methacrylate, containing 50–74% styrene, it was shown [145] that the dependence of the main thermodynamic properties of solutions, in toluene and ethyl methyl ketone, of fractionated specimens of these block copolymers, on the composition of the fractions, passes through a maximum at a styrene concentration of ~60%. In particular, the entropy of dissolution, heat of dilution, molecular dimensions, and the unperturbed length of the molecules of the block copolymers, calculated from viscosimetric data, have maximum values for the specimens containing 60% styrene. This phenomenon was related to the limiting intramolecular "separation into layers" of the homopolymeric sections of the block copolymer molecule as a result of their low compatibility in the given proportions. At the same time the values of the second virial coefficient and the Huggins constant are unaffected by change in the composition of the block copolymer, and this in turn can be attributed to the mutually cancelling influence of the two homopolymeric blocks of the same block copolymer molecule. The apparent dissociation constants of the block copolymers of acrylic acid with acrylamide were determined by electrometric titration [146] in 0.1 N carbonate-free sodium chloride solution, with 0.1 N sodium hydroxide solution. It was found that the acidity of this block copolymer is the same as that of polyacrylic acid.

In the study of the viscosity and light scattering of solutions of block copolymers of acrylonitrile and methyl methacrylate in mixed solvents [147], it was found that when benzene is added to a solution of the block copolymer in dimethylformamide there is a sharp decrease in viscosity and an increase in turbidity, continuing over a definite time interval. An analogous effect is produced by the addition of other precipitants to this solution. The critical concentration increases in the order $H_2O < CH_3COOH <$ $< C_2H_5OH < C_6H_6 < CCl_4 < (CH_3)_2CO$. The subsequent addition of dimethylformamide restores the viscosity of the system and decreases the turbidity, with considerable hysteresis. This change in the properties of the block copolymer solutions is due to the repeated formation of aggregates as a result of electrostatic interaction between the acrylonitrile units in the block copolymer chains. The use of the viscosity and light scattering of solutions of block copolymers in mixed solvents has been proposed for the determination of the composition and structure of block copolymers. The addition of acetonitrile to a benzene solution of the block copolymer of styrene with methyl methacrylate gives stable colloidal dispersions of the polymer as a result of the partial displacement of the chains of the polystyrene block while the chains of the polymethyl methacrylate block remain as it were dissolved in the solvent–precipitant mixture. Analogous dispersions can be obtained by peptising dry block copolymer; in this case it is found that the dimensions of the particles in the dispersion are related to the molecular weight of the block copolymer. A model has been proposed [148] relating the dimensions of the particles, the mean-square distance between the ends of the chains, and the molecular weight of the block copolymer.

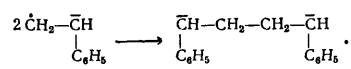
In a study of the vitrification temperature of block copolymers of acrylonitrile with methyl methacrylate [149], it was found that the value is intermediate between the vitrification temperatures of poly(acrylonitrile) and poly(methyl methacrylate), and depends to a marked extent on the structural arrangement of the monomer units in the polymer chain. This confirms the general hypothesis that the vitrification temperature of polymers is sensitive to the degree of structural order. The results of the studies showed that in this block copolymer the poly(acrylonitrile) block has a much greater influence on the properties of the block copolymer than the poly(methyl methacrylate) block.

2. Synthesis of Block Copolymers by Anionic Polymerisation

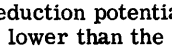
The simplest carbochain block copolymers can be synthesised by the "live" chain method proposed by Szwarc [150,151] and others [152]. In the case of styrene, anionic polymerisation can be carried out in the presence of the products of the addition of alkali metals to aromatic compounds in tetrahydrofuran. The resulting polymer molecule remains "live" during polymerisation until all the monomer is used up, as a result of which the "live" end may undergo polymerisation with new units of another monomer, added to the polymerisation system. Champetier [153] proposed the following mechanism for this block copolymerisation: naphthalene reacts with sodium or lithium to form a compound with component ratio close to 1. In tetrahydrofuran, capture of the electron of the sodium by naphthalene leads to dissociation of this compound to the Na^+ cation and the naphthalene radical-anion. In the presence of styrene, this radical-anion can act as an agent for the transfer of the negative charge to the styrene, with the formation of the styrene radical-carbanion.



Theoretically, there are two possible ways in which the polymerisation of styrene may begin under the influence of the styrene radical-carbanion — radical and anionic. Since in a medium of tetrahydrofuran the rate of anion polymerisation is much greater than that of radical polymerisation, however, and the styrene radical-carbanions have a tendency to combine at low temperatures by means of their radical ends with the formation of doubly-charged carbanions, in practice only anionic polymerisation takes place.



In the same paper Champetier states that the initiation of the polymerisation of the first monomer A by initiator is possible when the reduction potential of the initiator is higher or only slightly lower than the reduction potential of the monomer, since an equilibrium reaction of the type



takes place.

Initiation does not take place if the reduction potential of the initiator is appreciably lower than the reduction potential of the monomer. This also applies to the second stage of the synthesis of the block copolymer, that is, in order to obtain a block copolymer, it is necessary that the reduction potential of the polymer block be greater or only slightly less than the reduction potential of the second monomer. The block copolymers obtained with this condition usually consist of a central homopolymeric block (AAA), bounded on both sides by two different polymer blocks (BBB). If, however, the two monomers have fairly similar reduction potentials, it is possible to obtain a block copolymer whose main chain consists of several successive alternating homopolymer blocks AAA and BBB. A block copolymer with this structure was synthesised from styrene and isoprene [154] in tetrahydrofuran in the presence of the sodium naphthalenide as catalyst. Two series of block copolymers were obtained, with molecular weights 15 800 and 158 000 and the same molar ratio of homopolymeric blocks of styrene (A) to homopolymeric blocks of isoprene (B), but with different numbers and lengths of alternating blocks (A...AB...BA...AB...B). It was found that when the first (original) monomer is isoprene, the polydispersity of the block copolymers is greater, evidently due to the fact that the life of the polyisoprene chain is longer than that of the polystyrene chain.

Block copolymers of styrene with methyl methacrylate [155-157], containing about 46% styrene and 54% methyl methacrylate, are obtained by initiating the polymerisation of methyl methacrylate with "live" polystyrene at -70° in solution in tetrahydrofuran. To determine the molecular weight of the polystyrene blocks in these block copolymers, the growth of the "live" polystyrene chain in control experiments was terminated before the addition of methyl methacrylate and the light scattering of benzene solutions of the block copolymer was compared with that of solutions of the control specimen of homopolystyrene [158]. A combination of these methods and chemical analysis showed that the molecular weight of the polystyrene blocks is the same as that of the control homopolystyrene. When block copolymerisation was complete, no homopoly(methyl methacrylate) was detected, although about 50% of the polystyrene does not react; this is evidently due to the influence of deactivating impurities. Block copolymers of styrene and acrylonitrile were synthesised in analogous fashion [156,159]. Here it was found that acrylonitrile cannot form either a "live" polymer or a homopolymer. The solubility of these block copolymers in dimethylformamide increases with increase in their styrene content.

In the presence of sodium-naphthalene or sodium–biphenylide in tetrahydrofuran, "live" polymers may also be formed by 1,2-dihydronaphthalene and 2-vinylpyridine, and block copolymers of these compounds with styrene [160], containing up to five segments of homopolymer blocks, have been prepared. The viscosity of the resulting block copolymers is anomalously low, evidently due to the mutual incompatibility of the segments.

On the basis of the electron affinity of the monomers, Franta [161] studied the ability of monomers to form block copolymers under the influence of phenylisopropylpotassium of the "live" disodium tetramer of α-methyl-styrene in tetrahydrofuran in an atmosphere of argon at -80°. The monomers studied were arranged in the following order of increasing carbanion stability and ability to initiate the polymerisation of all subsequent monomers, with the formation of block copolymers: α-methylstyrene (1), styrene (2), isoprene (3), 2-vinylpyridine (4), 4-vinylpyridine (5), α-vinylnaphthalene (6), p-bromostyrene (7), methyl methacrylate (8), methacrylonitrile (9), methyl acrylate (10), acrylonitrile (11), and ethylene oxide (12). Block copolymers are formed in good yield by the reaction of "live"

polymers of (2) with (3)–(9) and (12), (3) with (12), (5) with (8), and (7) with (8). The polymerisation of styrene is not initiated by the carbanions of (7), (8), and (9), and the polymerisation of 4-vinylpyridine is not initiated by the carbanions of (8).

Other catalysts which are often used in anion polymerisation to obtain carbochain block copolymers are the alkyllithiums: methyllithium, ethyllithium, n-propyllithium, n-butyllithium, n-pentyllithium, and their mixtures[162], and also compounds of lithium with alicyclic or aromatic radicals[163]. These have been used to prepare block copolymers of styrene with methacrylonitrile and of styrene with acrylonitrile. Block copolymers of butadiene or piperylene [penta-1,3-diene (Ed. of Translation)] with styrene, or of piperylene with isoprene, were prepared in analogous fashion[164]. Of the block copolymers obtained in the presence of alkyllithiums, the block copolymer of styrene with isoprene has been studied in most details[165]. Comparison of the curves for the nephelometric titration of the block copolymer and a mechanical mixture of the homopolymers of styrene and isoprene, with the same composition as the block copolymer, together with comparison of their ultraviolet spectra, showed that the copolymer is a block copolymer. The quantitative composition of the block copolymer was studied by measuring the partial specific volumes, by measuring the refractive indices of films of the block copolymer, and by ultraviolet spectroscopy. The equilibrium sedimentation of the block copolymer in a density gradient was also studied[166]; for this purpose a solution of the block copolymer in a mixture of butyl chloride and dichloroethane was placed in the centrifugal field of an ultracentrifuge. When equilibrium was established, the traces of homopolymers were concentrated at the foot of the cell and at the meniscus, and the block copolymer, which has an intermediate density, collected in a narrow band at a certain distance x from the axis of rotation. The integral block copolymer concentration distribution close to x has the form of a gaussian curve, whose width is determined by diffusion and the polydispersity of the composition.

Anionic block copolymerisation can also be carried out in the presence of metallic lithium[167,168]. The reaction is carried out in tetrahydrofuran. An interesting feature is that the reaction appears to take place as a result of instantaneous growth of the radical-ion. Metallic sodium can also be used as catalyst for this polymerisation[169,170]. A method has been described[171] for preparing block copolymers using metallic sodium; a film of sodium is treated successively with the vapours of styrene and α-methylstyrene. The latter polymerises at the anionic end of the polystyrene with the formation of a live block copolymer radical. By repeating this operation it is possible to obtain a block copolymer with the required number of blocks. The softening temperature of the block copolymers is intermediate between that of a mixture of the homopolymers and that of a statistical copolymer of the same components, and decreases with increase in the number of blocks.

A method has been described[172] for preparing a block copolymer of ethylene with propene in the presence of a catalytic metal–Lewis acid ($TiCl_4$, $VOCl_3$) system. In this case also, polymerisation takes place by an anionic mechanism.

Stereospecific Ziegler–Natta catalysts[173] have also found extensive application in anionic block copolymerisation. For the most part these catalysts are used to obtain block copolymers of alkenes and their α-substituted derivatives.

The preparation of block copolymers of ethylene with propene with an unlimited number of homopolymer blocks of both monomers has been described[174]. To obtain these blocks of given length, it is recommended that each monomer be introduced into the polymerisation system alternately or after strictly defined time intervals[175] or until the vapour pressure of a given monomer decreases during polymerisation to a definite required value[176]. Another method for preparing these block copolymers[177] is based on the fact that the catalyst at the end of the growing chain does not lose its activity. In this method, as the polymerisation of ethylene is nearing completion, propene is added to the polymerisation system to undergo block copolymerisation with the polyethylene. This process may be repeated indefinitely to give block copolymers with a predetermined number of homopolymer blocks of both monomers. Increase in the total duration of the reaction gives block copolymers with a high characteristic viscosity, and increase in the propene content gives a polymer with higher density.

It has been shown possible[178] to apply rheological analysis to block copolymers of this type. Analogous methods may be used to obtain block copolymers of pent-1-ene, oct-1-ene, cyclohexene, butadiene, or isoprene with allyl bromide or chloride, methallyl chloride, isoprene, butadiene, styrene, but-1-ene, oct-1-ene, and chloroprene[179], and of ethylene with but-2-ene.[180] Infrared spectroscopy and X-ray diffraction showed[181] that block copolymers of acrylonitrile with vinyl acetate, methyl methacrylate, or styrene have a lower crystallinity than the homopolymers of these monomers, obtained under analogous conditions. A number of published facts[182] indicate that when certain catalytic systems such as $TiCl_4 + LiAlR_4$ or $VOCl_3 + AlR_2Cl$ are used, growth of the macromolecules continues for several days. These "long-lived" macromolecules were used for the synthesis of block copolymers of ethylene with propene and of ethylene with but-1-ene, with different types of distribution of the monomer units in the blocks. By varying the method of preparing the block copolymers, it was possible to obtain polymers with different structures, from crystalline to amorphous. The molecular conformation of the polymer and its hydrodynamic and mechanical properties were studied[183] for the case of the block copolymer of styrene with isoprene in the ratio 4 : 5. The molecular configuration of this block copolymer was investigated in the course of a study of the characteristic viscosity, diffusion, and sedimentation of the polymer in benzene, which is an effective solvent for both homopolymeric blocks, and also in ethyl methyl ketone and octane, which are selective solvents for the polystyrene and polyisoprene blocks respectively. It was shown that in the selective solvents, the insoluble blocks form globules but are retained in solution by the blocks which are "soluble" in the given solvent. This leads to a departure from the relationship connecting $\langle r^2 \rangle^{1/2}$ with $[\eta]$ and D, derived by Flory for flexible chain macromolecules, whereas this relationship is satisfied completely for the same block copolymer in benzene. Study of films of block copolymers obtained from selective solvents showed that the globular structure of the "insoluble" blocks is preserved completely after removal of the selective solvent, so that the film of block copolymer, obtained from solution in octane, behaves like rubber with a chemically bound filler, and the film obtained from solution in ethyl methyl ketone behaves like plasticised polystyrene.

The polymerisation of diazo-compounds in the presence of boron trifluoride or its derivatives takes place by a mechanism identical with that of the polymerisation of alkenes in the presence of Ziegler–Natta catalysts.

The macromolecules of the type $X_2B-(CHR)_n-X$ formed as a result of polymerisation are able in turn to initiate the polymerisation of freshly prepared diazo-compounds with the formation of block copolymers of the type $X_2B-(CHR)_n-(CHR')_m-X$. A polymerisation mechanism has been proposed[184], similar to that of the polymerisation of ethylene in the presence of alkylaluminiums, involving coordination of the diazoalkanes with the boron catalyst and subsequent migration of the groups initially bound to the boron atom. Analogous derivatives containing boron were observed in the reactions of diboranes with dialdehydes and ketones. Alkylene oxides can also react with diborane with the formation of products of the type $H_2B(OCH_2CHR)_nH$ and $HB\begin{smallmatrix}(OCH_2CHR)_xH\\(OCH_2CHR)_yH\end{smallmatrix}$. These reactions, as noted above, are similar to the polymerisation of alkenes, catalysed by alkylaluminiums, since both reactions include the stepwise anionic growth of the metal–alkyl chain. Since the diazoalkane has much higher nucleophilic activity than ethylene, it can, unlike ethylene, react with alkylborons. Alkylaluminiums in turn have a higher electrophilic activity than the corresponding alkylborons, so that it is to be expected that diazo-compounds will undergo block copolymerisation when initiated with alkylaluminiums more readily than the corresponding alkenes.

An ionic mechanism involving anionic and cationic polymerisation stages was proposed[185] for the preparation of block copolymers of α-methylstyrene and isobutene with acrylonitrile and with acrylates. The α-methylstyrene or isobutene is polymerised by a cationic mechanism with the formation of positive ions at the ends of the growing chains. Acrylonitrile or acrylates in turn polymerise by an anionic mechanism to give macromolecules containing terminal negative ions. The reaction of these growing macromolecules with ions of opposite sign at the ends of the chains gives the corresponding block copolymers.

Anionic polymerisation is also used to prepare the so-called stereo-block copolymers, consisting of polymeric molecules containing alternating, relatively long polymeric fragments with different spatial configurations, formed from the same monomer. These macromolecules may consist of isotactic and atactic segments, or of isotactic segments alone, with different spatial configurations. The mechanism of their formation was examined by Natta[186] on the basis of the assumption that two processes take place simultaneously — chain growth and a process in which inversion of configuration takes place. In practice, amorphous polymers, regarded as atactic, may contain very short stereo-blocks[187], which have not yet been isolated in pure form. The stereo-block copolymers of α-alkenes, with relatively long segments with definite spatial configurations, are usually isolated from a mixture of the amorphous and crystalline polymers by extraction with selective solvents[188,189] with increasing solvent power for the given polymer. In this way it is possible to separate the amorphous polymer and stereo-block copolymers with different crystallinities[190-193]. Natta[194] showed, however, that the fractionation method is not always applicable to the separation of stereo-block copolymers of propene, since the solubility of the polymer usually depends not only on the degree of crystallinity but also on its molecular weight and structure. The separation of stereo-block copolymers differing only in their degree of crystallinity can be carried out successfully on a chromatographic column with a substrate of isotactic polypropene. In a study of the mechanical properties of the stereo-block copolymer of propene[195], it was found that at a high degree of isotactic character, when the macromolecule contains very small atactic segments, the fibres obtained from a melt of the block copolymer have a high strength.

A stereo-block copolymer of methyl methacrylate, consisting of alternating isotactic and atactic or syndiotactic and atactic polymeric blocks is obtained by the radical and anionic polymerisation of methyl methacrylate at low temperatures[196-198]. The isotactic-syndiotactic stereo-block copolymer of methyl methacrylate is obtained by polymerising methyl methacrylate in the presence of 9-fluorenyllithium at -70° in a medium of toluene[199]. This type of stereo-block copolymer crystallises readily[200,201] from pentyl acetate, heptan-4-one, and octan-3-one. The stereo-block copolymer of styrene can be isolated by extracting polystyrene synthesised in the presence of titanium-containing organometallic catalysts and washed beforehand with dry diethyl ether[202]. A method has been described for preparing linear stereo-block copolymers of propene, but-1-ene, and pent-1-ene, with macromolecules containing isotactic crystallising sections with asymmetric carbon atoms with the same spatial configuration, and also non-isotactic non-crystallising sections[203,204]. In the isolation of these stereo-block copolymers, the resulting mixture of polymers is separated by extraction with selective solvents, which dissolve first the non-isotactic polymers and then the stereo-block copolymers with gradually-increasing degrees of crystallinity. It has been reported that stereo-block copolymers can also be obtained from the dialkenes butadiene and isoprene[205]. It was suggested[206] that under the conditions of the stereospecific polymerisation of isobutyl vinyl ether[207,208], a stereo-block copolymer whose macromolecule consists of *d*- and *l*-isotactic segments and several atactic segments, distributed along the polymer chain, is also formed.

In the study of stereo-block copolymers, the proportion of isotactic and syndiotactic fragments can be determined by infrared spectrocopy[209,210] and the three-dimensional structure as a whole can be determined by measuring the heats of fusion[211,212] or by nuclear magnetic resonance studied on instruments with a high resolving power[213,214]. The three-dimensional structure of the stereo-block copolymer of styrene can also be determined from the difference in the rates of hydrolysis of the benzanilides of the atactic and isotactic segments of the polymer[215], which are readily obtainable from polystyrene and consist of the polyvinyl benzanilides with the corresponding spatial configurations.

3. Synthesis of Carbochain Block Copolymers by the Combination of Polymer Blocks, Containing Chemically Active Terminal Groups, by Means of Low-Molecular Bifunctional Compounds

To obtain homochain polymer blocks containing chemically active terminal groups, Bamford and Jenkins[216] proposed that the polymerisation of the original monomer be initiated using organic compounds containing two azo-groups and a functional group capable of reacting with hydroxyl or carboxyl groups. By initiating the polymerisation of styrene, acrylonitrile, and methyl methacrylate with γ,γ'-azo-γ-cyanovaleric acid or δ,δ-azo-δ-cyano-n-pentanol, they prepared[217] homopolymeric blocks of styrene, acrylonitrile, and methyl methacrylate containing carboxyl or hydroxyl groups. To obtain macromolecules with a relatively low molecular weight and relatively high concentration of active terminal groups in the mixture of poly-

mer homologues, they suggested the use of an apparatus which makes it possible to carry out this process continuously. Block copolymers can be synthesised from the macromolecules with active terminal groups prepared in this way, by two methods: (1) by direct combination of two macromolecules, or (2) by the combination of two macromolecules by means of low-molecular bifunctional compounds such as decamethylene glycol.

In a study of the resulting block copolymers, Bamford and Jenkins[218] found that the molecular-weight distribution of these block copolymers is a function of the molecular-weight distribution of the original homopolymer blocks, the duration of the reaction, and the chemical properties of the reactive terminal groups. Using the method of Laplace transformations, they derived a general equation which makes it possible to use the measured characteristic viscosity to reach conclusions regarding the ratio of the final and initial mean polymerisation coefficients.

III. CARBO-HETEROCHAIN BLOCK COPOLYMERS

Carbo-heterochain block copolymers, like carbochain block copolymers, can be obtained by various mechanochemical methods. The degradation of the polymer chains for the formation of reactive macroradicals is achieved using various grinding assemblies[219-222], by means of the electrohydraulic effect[46,47,223], and also by the freezing and subsequent melting of aqueous solutions of the polymers[224-226].

Carbo-heterochain block copolymers can also be obtained by anionic or radical polymerisation, by polycondensation, and by combining carbochain blocks with heterochain homopolymeric blocks.

1. Synthesis of Carbo-Heterochain Block Copolymers by Ionic Polymerisation

By analogy with the synthesis of carbochain block copolymers, carbo-heterochain block copolymers can be synthesised by Szwarc's "live" chain method. This method has been used to synthesise block copolymers of isoprene with ethylene oxide[161], of styrene with ethylene oxide, and of styrene with propene oxide[227]. This gives block copolymers of two types: polystyrene–poly(alkylene oxide) and poly(alkylene oxide)–polystyrene–poly(alkylene oxide). The polymeric products formed in the reaction always contain the alkylene oxide homopolymer in quantities corresponding to 46.4–73.6% of the total poly(alkylene oxide) content[228], probable due to the presence, in the polymerisation system, of traces of moisture, alkali, or oxygen, which terminate the growth of the block copolymer chain. In a study of the block copolymer of the second type in the block copolymer–water–ethylbenzene system[229], it was found that in these systems the block copolymers form mesomorphic gels resembling the nematic structures in the systems formed by water with low-molecular soaps. Study of the resulting birefringent structures by means of X-rays and the polarisation microscope showed that the hydrophobic polystyrene blocks, in the mixture with ethylbenzene, are localised with the formation of a hexagonal liquid-crystalline lattice in cylindrical regions with parallel orientation; the space between these regions is filled with a mixture of the hydrophilic poly(ethylene oxide) blocks and water. Each of the separate homopolymer blocks of the block copolymer has the configuration of a statistical coil. The equilibrium diagram shows clearly an immiscibility zone in which the gel is present in equilibrium with the isotropic liquid. At low concentrations of block copolymer, separation of the phases also takes place, and the aqueous and ethylbenzene layers can be separated by centrifuging. Mesomorphic gels are also formed in binary systems if the solvent is an effective solvent for the poly(alkylene oxide) blocks and an ineffective solvent for the polystyrene blocks, or vice versa. The gels may be nematic or smectic, depending on the nature of the solvent, but in both cases they are extremely stable.

The influence of the nature of the solvent on the structure of the mesomorphic gels of the block copolymers of styrene with ethylene oxide have also been studied by the method involving the scattering of X-rays at small angles in nitromethane, which is a solvent for the poly(ethylene oxide) and a precipitant for polystyrene, and in butyl phthalate, which is a solvent for polystyrene and a precipitant for poly(ethylene oxide)[230]. Mesomorphic gels of the block copolymer of styrene with ethylene oxide are formed in solutions in acrylic acid, which is a solvent for poly(ethylene oxide) and a precipitant for polystyrene, and in methyl methacrylate, which is a solvent for polystyrene and a precipitant for poly(ethylene oxide). When these systems are iradiated with ultraviolet light[231], the monomer present in the system polymerises in the presence of the mesomorphic phase, ensuring the production of a solid protective mesomorphic gel structure and forming a copolymer with an ordered structure. The irradiation of the "block copolymer of styrene with ethylene oxide–acrylic acid" system gives a copolymer of acrylic acid, whose gel has a cylindrical structure up to a concentration of block copolymer in the system equal to 90%, and a lamellar structure at other concentrations. The "block copolymer of styrene with ethylene oxide–methyl methacrylate" system under analogous conditions forms only a lamellar structure. The cylindrical structures were evidently formed by the aggregation of "cylinders" of polystyrene blocks surrounded by a solution of the poly(ethylene oxide) blocks, and the lamellar structure by a combination of alternating layers of "crystalline" poly(ethylene oxide) blocks and a polystyrene blocks in solution respectively.

Anion polymerisation can also be used to prepare carbo-heterochain block copolymers with general formula:

$$CH_3(C_2H_4)_n C(R')(R'')O[CH_2CH(R''')O]_m CH_2CH(R''')OH,$$

where R′ and R″ are alkyl groups with 1–4 carbon atoms, R‴ = H, CH_3, or C_6H_5, n = 30–250, and m = 1–70. These block copolymers are obtained by the reaction of polyethylene telomers, modified by monohydrie aliphatic alcohols or dialkyl ketones, with alkylene oxides in the presence of Na, Ce, Li, K, $NaOCH_3$, NaOH, or KOH in the molten state at 110–200° or in aqueous emulsion[232]. The block copolymer of acrylonitrile with ethylene oxide is obtained by polymerising acrylonitrile under the influence of the sodium salt of polyethylene glycol[233]. The composition of this block copolymer can be studied by infrared spectroscopy.

2. Synthesis of Carbo-Heterochain Block Copolymers by the Combination of Polymer Blocks, Containing Chemically Active Terminal Groups, by Means of Low-Molecular Bifunctional Compounds

Carbo-heterochain block copolymers of the polystyrene–poly(ethylene oxide)–polystyrene and polystyrene–poly(ethylene oxide) types are prepared by the combination of

polyhydroxyéthylene glycol with polystyrene containing one or two terminal acid chloride groups and prepared by the reaction of "live" polystyrene with phosgene[228].

It is also possible to synthesise carbo-heterochain block copolymers based on 2,2-di-(4-hydroxyphenyl)propane polycarbonate. These are prepared by linking polystyrene with low-molecular 2,2-di-(4-hydroxyphenyl)propane polycarbonate containing terminal hydroxyl groups[234]. Polycarbonate blocks with low molecular weight, controllable within narrow limits, are obtained by varying the concentration of the original substances and the reaction temperature, and polystyrene blocks with terminal hydroxyl groups are prepared by hydrolysing a polymer obtained in the presence of benzoyl peroxide and containing terminal benzoxy-groups. The presence of flexible blocks in the block copolymer chain facilitates ordering of the polycarbonate, which forms flexible polymers with a high melting point. It was found[235] that during the bulk polymerisation of a mixture of styrene with β-propiolactone in the presence of an initiator of the radical type, the product is a copolymer, hydrolysis of which, followed by treatment with poly(ethylene oxide), gives a carbo-heterochain block copolymer.

3. Synthesis of Carbo-Heterochain Block Copolymers by Radical Polymerisation

A method was recently developed for preparing polymeric peroxide initiators[236], making it possible to carry out carbo-heterochain block copolymerisation by the radical-polymerisation method. These initiators are prepared by polymer-analogue transformations from aliphatic or aromatic polyesters containing terminal carboxyl or acid chloride groups at the surface of separation between the two phases. On thermal decomposition, these initiators form macroradicals capable of initiating the block copolymerisation of vinyl monomers, which polymerise by a radical mechanism. This method has been used to synthesise a block copolymer of a polyester of hydroxyheptanoic acid with poly(methacrylic acid). Unlike poly(methacrylic acid), the resulting block copolymer is fusible, soluble in a mixture of acetone and methanol, and insoluble in water.

An extremely promising method for the production of fibres involves the use of carbo-heterochain block copolymers which may be partly or completely crystalline according to the crystallising ability of the homopolymer fragments which alternate regularly in the main chain of the block copolymer. The carbo-heterochain block copolymer of acrylonitrile with 10–40% of compounds such as poly(vinyl alcohol), poly(ethylene oxide), starch, cellulose, and poly(acrylic acid) can be used[237] to prepare readily dyed fibres using ordinary shaping methods.

IV. HETEROCHAIN BLOCK COPOLYMERS

Heterochain block copolymers were first found in natural macromolecular compounds. In a study of silk fibroin, consisting of a polypeptide chain[238], it was found that the amino-acids are arranged in the chain in an ordered fashion. X-Ray diffraction study of the same silk fibroin[239] established that its molecule, with molecular weight ~30 000, consists of three segments of an ordered structure with molecular weight ~7000, separated by amorphous segments with molecular weight ~5000. This indicated that silk fibroin is a natural heterochain stereo-block copolymer. A number of block copolymers of cellulose were prepared by synthesis[240]. It was found[241] that substitution in cellulose under heterogeneous conditions in most cases gives heterochain block copolymers containing large segments of unchanged glucose residues, located chiefly in crystalline regions. The glucose residues in the amorphous regions are very sensitive to the action of substituents. X-Ray structural analysis shows that up to a degree of substituion in the cellulose equal to 25–35%, no changes are observed in the crystalline regions. The resulting block copolymer combines the properties of rigidity and strength, associated with the crystalline regions, with elasticity and flexibility, asociated with the substitution in the amorphous regions.

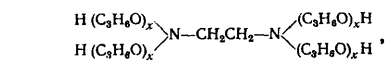
Synthetic heterochain block copolymers can be obtained by ionic polymerisation, polycondensation, the combination of heterochain polymeric blocks containing chemically active terminal groups, inter-phase polycondensation, and exchange reactions.

1. Synthesis of Heterochain Block Copolymers by Ionic Polymerisation

This method has been used to prepare heterochain block copolymers of formaldehyde with various polymeric blocks containing active terminal hydroxyl, sulphydryl, carboxyl, or primary amino-groups[242]. For example, the polymerisation of 99% pure formaldehyde in the presence of dimethyldialkylammonium hydroxide and poly(tetramethylene glycol) with molecular weight ~7000 gives a block copolymer containing 73% poly(methylene oxide) units. This block copolymer is less crystalline but has a higher impact strength than the formaldehyde homopolymer[243]. The preparation of block copolymers of diisocyanates or bisepoxy compounds with linear polyesters containing terminal hydroxyl groups has been described[244]. X-Ray structural analysis of these block copolymers indicates the presence of crystalline regions with structures identical with that of the crystallites of the homopolymers. Some block copolymers with low glass points and low degrees of crystallinity, such as poly(ethylene terephthalate)–poly(ethylene adipate), are rubberlike materials with high strength. The block copolymers of ethylene oxide with propene oxide[245] have found extensive application as non-ionic detergents. A poly(propene oxide) block containing a terminal hydroxyl group is used as the original hydrophobic fragment of the block copolymer chain[246–248]. When ethylene oxide is added to this macromolecular glycol, its terminal groups initiate block copolymerisation with the formation of a block copolymer with general formula:

$$HO-(CH_2CH_2O)_x-(C_3H_6O)_y-(CH_2CH_2O)_xH.$$

The physical properties of these block copolymers may be varied over a wide range to give mobile liquids (40% ethylene oxide), waxy products (50% ethylene oxide), and hard solids (70% ethylene oxide). Analogous methods can be used to prepare block copolymers of propene oxide and ethylene oxide with ethylenediamine[249], since the reaction of propene oxide with ethylenediamine gives a macromolecular compound with general formula



whose terminal groups are able to initiate the polymerisation of ethylene oxide with the formation of a block copolymer.

Block copolymers of alkene 1,2-oxides, with general formula $R''(RCHRCHO)_n-(R'CHR'CHO)_mH$, where R and R' represent the H atom or a hydrocarbon radical, and R'' the radical in the catalyst molecule, are obtained in two stages[250]. In the first stage, the polymerisation of the alkylene oxide $\overline{RCHRCRO}$ is initiated by organometallic catalysts, and in the second stage the polymerisation of the other alkene oxide $R'\overline{CHR'CHO}$ is initiated by the primary polymer block containing active terminal groups. When alkaline or acidic catalysts are used in the first stage of the block copolymerisation, it is possible in analogous fashion to obtain block copolymers of alkyl glycidyl esters with ethylene oxide. Block copolymers of this type have found application as surface-active agents[251]. It was found that the surface-active properties of these block copolymers deteriorate sharply with increase in the length of the lateral groups.

In a study of block copolymers of the poly(ethylene oxide)–poly(propene oxide)–poly(ethylene oxide) type[252], it was found that in benzene solution these copolymers form inclusion compounds with urea and thiourea. Viscosimetric determination of the molecular weights of these inclusion compounds showed that there is an appreciable fractionating effect.

The ion polymerisation method was also used to prepare heterochain stereo-block copolymers[253]. For example, the polymerisation of acetaldehyde in the presence of partly hydrolysed aluminium alkoxide gave a stereo-block copolymer of acetaldehyde, whose structure was confirmed by solubility data, infrared spectroscopy, and X-ray structural analysis. This stereo-block copolymer is less elastic than atactic amorphous polyacetaldehyde. Its solubility is intermediate between the solubilities of the crystalline and amorphous polymers[254].

2. Synthesis of Heterochain Block Copolymers by Polycondensation

This method for preparing the heterochain block copolymers has been very little studied, and is used chiefly for modifying the properties of polyesters used in the production of synthetic fibres. It has been used to prepare block copolymers of ethylene terephthalate with poly(ethylene oxide) by heating a mixture of dimethyl terephthalate, ethylene glycol, and poly(ethylene oxide) at 200–275°, in the presence of PbO. Study of the properties of this block copolymer[255] showed that the introduction of poly(ethylene oxide) blocks with molecular weight 1000–6000 into the polymer increases the hydrophilic character of the polymer, its flexibility, and the ease with which it can be dyed. The degree of crystallinity, strength, and ductility shown by this block copolymer, are almost the same as those for polyethylene terephthalate, but the stability to the action of ultraviolet light is much lower. At concentrations of poly(ethylene oxide) in the block copolymer up to 20%, the mechanical properties deteriorate[256] due to the decreased concentration of crystalline fraction in the fibre.

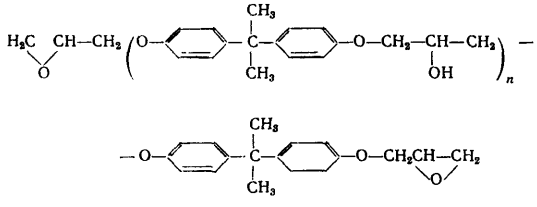
3. Synthesis of Heterochain Block Copolymers by the Combination of Polymer Blocks Containing Chemically Active Terminal Groups

This method, involving the introduction of flexible and elastic blocks of one polymer into the main chain of another polymer with a rigid structure, can be used to modify macromolecular compounds such as polycarbonates[257]. As a result of the presence of these blocks, which alternate regularly in the main chain of the block copolymer, the final product is also elastic. For example, the block copolymer formed by the combination of polycarbonate blocks with poly(tetramethylene oxide) is an elastomer[234]. More frequently, however, the polymeric blocks are joined by means of low-molecular bifunctional compounds such as diisocyanates, with the formation of heterochain polyester–urethane block copolymers[258,261].

The methods for preparing these block copolymers are varied. For example, a polyester with a molecular weight of several thousand, obtained by the polycondensation of adipic acid with ethylene glycol, is treated with an excess of diisocyanate to join the polyester blocks. The isocyanate groups formed at the ends of the chain are in turn capable of reacting with water, glycols, or diamines, with the formation of substituted ureas[262]. Analogous methods are used to prepare block copolymers of poly(ethylene terephthalate) with poly(ethylene succinate), poly(ethylene adipate), poly(ethylene azelaate), poly(ethylene sebacate), poly(ethylene phthalate), poly(ethylene isophthalate), and poly(diethylene adipate)[263]. Tetramethylene diisocyanate is used as linking agent. The properties of these block copolymers differ considerably, depending on the chemical nature of the original polyester blocks. The degree of crystallinity of the reactants and products can be determined by X-ray structural analysis and from the temperature of the second-order transformation.

It is possible to obtain a rubberlike elastic heterochain block copolymer suitable for the production of fibres and films[264] by using as the original polymer blocks, polyesters prepared by the polycondensation of glycol with an aliphatic dicarboxylic acid or with an asymmetric aromatic dicarboxylic acid and poly(ethylene terephthalate), and by using tetramethylene diisocyanate as linking agent. The preparation of block copolymers by the combination of statistically mixed polyesters using diisocyanates has also been described[262]. These block copolymers have a lower strength than the analogous block copolymers consisting of two components, evidently because of the irregularity of the polyester chain, resulting from the introduction of a third component into the polyester block[265]. The use[266] of symmetrical aromatic diisocyanates as linking agents instead of aliphatic diisocyanates improves the physical properties of the resulting block copolymer. With increase in the "diisocyanate : polyester" ratio, the molecular weight of the heterochain block copolymer increases, with a corresponding increase in the viscosity of the dilute solutions, the Mooney plasticity, and the softening temperature. It was found[267] that in order to obtain polyester-urethane block copolymers with increased elasticity it is best to link the original polyester blocks by means of diisocyanates with three alkyl substituents. The physical properties of these block copolymers are also influenced to a marked extent by the crystallinity of the original polyester blocks[268]. For example, polyethylene terephthalate and polyethylene adipate are crystalline, and the physical properties of block copolymers based on these compounds are almost identical with those of the homopolymers. If, however, the crystallinity of one of these blocks is broken down, for example, by the introduction of a non-crystalline segment such as poly(propene adipate), the impact strength of the block copolymer increases, but all the other mechanical properties deteriorate, in almost direct proportion to the concentration of added polymer block, which acts as an internal

plasticiser. Heterochain block copolymers can also be obtained from epoxide resins of the type



(synthesised by the usual methods and containing active terminal epoxy-groups[269]) by the reaction with phenol–formaldehyde and urea–formaldehyde resins, polyamides, etc. Block copolymers of this type, prepared by the reaction of ED-5 and ED-6 with dimethylresorcinol resin, are used to impregnate glass fibres for the production of glass-fibre-reinforced plastics. Lacquer from this block copolymer, and glass fabric impregnated with it, remain stable for 2–2.5 months[270]. The fusion of phenol–formaldehyde and other polycondensation resins with polyesters, and also the treatment of Novolaks first with a polyhydric alcohol and then with a polybasic acid, was used by Petrov to obtain a number of heterochain block copolymers, which he called joint resins[271].

4. Synthesis of Heterochain Block Copolymers by Inter-Phase Polycondensation

Study of inter-phase polycondensation showed that this method can be used to prepare macromolecular compounds for the synthesis of heterochain block copolymers[272].

The block copolymers are prepared by the reaction of polymeric blocks containing terminal acid chloride and hydroxyl groups[273] at the phase boundary between two immiscible solvents[274]. The preparation of analogous block copolymers by the reaction of polyester blocks containing terminal hydroxyl groups with a mixture of the acid chlorides of dicarboxylic acids and diphenols has been described[275]. Similar block copolyesters[276] can be prepared by the joint condensation of two polyesters, for example, poly(ethylene terephthalate) and poly(ethylene isophthalate)[277].

5. Method Based on Inter-Chain Exchange Reactions

When two homopolyesters are fused together, a statistical copolymer is obtained[278]. In a study of the inter-chain reaction between polyester macromolecules, Korshak and coworkers[279] established that the process involves degradation and intermolecular exchange, as a result of which block copolymers are formed as intermediate products. This work enabled a number of authors to prepare various block copolymers by exchange reactions[280]. The use of CaO as catalyst for the reaction was proposed[281]. In analogous fashion, Flori[273] prepared block copolyesters using macromolecules containing terminal acid chloride and hydroxyl groups as original homopolyester blocks. In this case the formation of the block copolyesters most probably takes place both by the interaction of the active terminal groups of the polyesters and by the inter-chain exchange reaction. To increase the ease with which the fibres based on poly(ethylene terephthalate) can be dyed, Kresse[282] used exchange reactions to synthesise a number of block copolyesters of poly(ethylene terephthalate). In a study of the reaction conditions, he found that one of the decisive factors influencing the rate of redistribution is the viscosity of the components of the block copolycondensation Beginning with the formation of macromolecules of definite magnitude, the exchange reactions proceed predominantly by an intermolecular exchange mechanism; the block copolyester formed at the start of the reaction is converted into a mixed polyester in the subsequent stages of the reaction. The formation of block copolyesters in the poly(ethylene terephthalate) macromolecule was proved by extracting the products of the joint polycondensation. A fibre capable of undergoing subsequent orientation was formed from the resulting block copolyesters.

Mixed polyamides have been prepared in analogous fashion by fusing two polyamides together[283]. It is possible that when two different polyamides are fused together, exchange reactions take place, and the formation of the mixed polymers passes through a stage involving the formation of block copolymers[284]. Experimental confirmation of this suggestion was found in work by Ayers[285]. In a study of the formation of the statistical copolyamide based on nylon-6,6 and nylon-6,10 by distribution chromatography on paper, Ayers showed that formation of the block copolymers begins approximately half an hour after the start of the reaction, and that in the subsequent reaction these block copolymers are completely converted into the mixed polyamide. More detailed study of this reaction[286] showed that as the mixture of polyamides is heated there is a decrease in the temperature of flow and an increase in the solubility and tensile strength. The block copolymers formed in the reaction have a comparatively short life, of the order of 3–5 h. Analogous results were obtained in a study of inter-chain reaction for the case of the preparation of a mixed polyamide from poly(hexamethylene adipamide) and poly(hexamethylene sebacamide)[287]. The rate of the inter-chain reaction is increased considerably by the addition of small quantities of hexamethylenediammonium adipate, which catalyses side reactions. This catalyst also accelerates the subsequent conversion of the intermediate block copolymer into the mixed polyamide[288]. Inter-chain reaction has also been used to prepare heterochain block copolymers of polyamides with various thermosetting resins[289]; for this purpose the mixture of polyamide and epoxide resin is heated at 240–290° in the presence of t-butyl peroxide. When poly(aminotriazole) blocks are heated[290], only very stable block copolymers are formed, and on subsequent heating these are converted into a mixed polymer. The authors attribute this to the fact that in this polymeric system there is no inter-chain exchange reaction and the block copolymers are formed only by the reaction of the terminal groups of the homopolymers. Inter-chain reaction was recently used[291] to give a new type of heterochain block copolymer, consisting of mixed polyamido-esters. Polymeric products of this type are of considerable practical interest, since they open up the possibility of preparing polymers with a new combination of properties, based on previously prepared polymers. The formation of these mixed polymers in the first stage of the process, as in the case of mixed polyamides, is said to pass through a stage involving the formation of block copolymers, which apparently can be isolated in pure form under suitable conditions.

Modern methods of organic synthesis are making it possible to extend considerably the number of block copolymers. In addition to the synthesis of new block copolymers, it is necessary to pay particular attention to the

study of the dependence of the properties of block copolymers on their composition, the magnitude and number of the blocks, the sequence of the blocks, etc. The elucidation of this dependence will make it possible to achieve deliberate control of the synthesis of block copolymes and to obtain polymers with a desired range of properties.

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PROGRESS IN THE CHEMISTRY OF THE CARBODIIMIDES

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1. INTRODUCTION

The carbodiimides form a class of organic compounds the membership of which is determined by the presence of the carbodiimide grouping $-N=C=N-$. The general formula of the carbodiimides may be represented as follows:

$$R-N=C=N-R',$$

where R and R′ are alkyl or aryl groups.