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Block Copolymers of the Polycondensation Type

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A new class of block copolymers, namely block copolymers of the polycondensation type, is considered. A general indication of the methods of synthesis and structures of such block copolymers is given and the available information about different examples of block copolymers of the polycondensation type is surveyed.
The bibliography includes 174 references.

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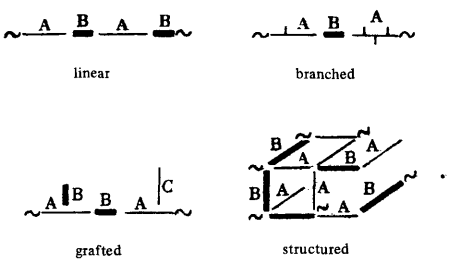
I. INTRODUCTION

The majority of the block copolymers known at this present time have been obtained by polymerisation methods[1-6], but in recent years an increasing number of studies have been devoted to block copolymers synthesised with the aid of polycondensation processes[7,8].

A separate examination of block copolymers of the polycondensation type merits attention for a number of reasons. 1. Virtually any homopolymer, of either polymerisation or polycondensation type, may be used as the corresponding oligomer with terminal functional groups in polycondensation reactions leading to the formation of block copolymers. The synthesis by polymerisation methods of oligomers having terminal functional groups capable of condensation is much simpler and technologically more effective than the synthesis by polycondensation methods of oligomers having terminal functional groups capable of polymerisation. Thus the synthesis of oligomers of the first type leads to considerable possibilities, realisable in practice, for the synthesis of block copolymers containing simultaneously polymer blocks of the polymerisation and polycondensation types. 2. In contrast to block copolymers of the polymerisation type, block copolymers of the polycondensation type can contain blocks of a wide variety of different kinds: aliphatic and aromatic, flexible and rigid, hydrophilic and hydrophobic, unsaturated and saturated, organic and inorganic, etc. 3. In most instances block copolymers of the polycondensation type are multiblock copolymers with a controllable length of blocks, whereas block copolymers of the polymerisation type are mainly two- and three-block copolymers with a poorly controllable length of blocks. The transition to the multiblock structure of block copolymers in which microphase separation occurs is accompanied by the formation of a more perfect physical network owing to the formation of a large number of domains consisting of highly fusible blocks, their more uniform distribution throughout the bulk of the polymer, and the involvement of the same macromolecule in the construction of a large number of domains. The controllable length of blocks permits the development of a stable technological manufacturing process for block copolymers. 4. Finally, perhaps the most significant factor is the successful development, to a large extent owing to the studies by V.V.Korshak and his school, of the theory of irreversible (non-equilibrium) polycondensation[9], which laid extensive foundations for the synthesis of block polymers of the polycondensation type. This refers primarily to acceptor-catalytic polycondensation, the mild conditions for the occurrence of which permit the synthesis of block copolymers with virtually complete suppression of the exchange processes and also lead to the possibility of the formation of block copolymers directly from the monomers[10,11].

II. METHODS OF SYNTHESIS AND STRUCTURE OF BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

Block copolymers of the polycondensation type include block copolymers the last stage in the formation of which is a polycondensation reaction. Such copolymers can be linear, branched, grafted (graft block copolymers), and structured:



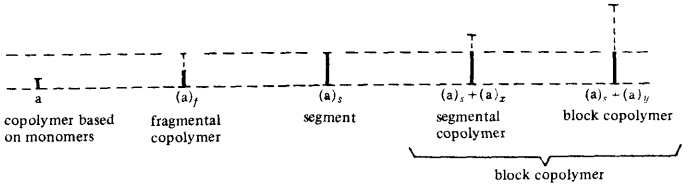
Linear block copolymers, to the consideration of which the present review is devoted, have been most thoroughly investigated at the present time.

Linear block copolymers are copolymers whose macromolecules consist of alternating blocks of homopolymers or statistical copolymers differing in composition or structure[12]. The concept of the "block" implies a relatively long sequence of elementary units of the polymer, whose length is equal to or greater than the length of the macromolecular segment which is a statistical element of the hypothetical polymer chain adequately simulating the physical properties of the macromolecule[13]. For this reason, terms such as "segmented (segmental) copolymers" and "block copolymers" are used simultaneously in the literature. The first term is frequently applied to segmented polyurethanes[12-15], where the molecular weights of the blocks do not exceed several thousand.

These are short-block copolymers, so that the number of blocks in their macromolecules is considerable. The second term, "block copolymers", is more applicable to long-block copolymers. The molecular weights of the constituent blocks in such copolymers can range from several to tens of thousands. The number of blocks in the macromolecules of polymers of this kind may vary from two (the minimum value for block copolymers) to several tens. Evidently, when the lengths of the blocks in the copolymer are similar to the length of the geometrical segment of the macromolecule, the terms "segmental copolymer" and "block copolymer" become synonymous.

Copolymers containing sequences of elementary units whose length is less than that of the geometrical segment of the macromolecule cannot be regarded as block copolymers; they can be called fragmental copolymers. These copolymers are formed when bifunctional fragmental compounds, consisting of more than one repeating elementary unit and whose chain length is less than that of the segment, are used. The introduction of such a compound into the copolymer macromolecule is equivalent to the introduction into the latter of a chain fragment of another polymer. However, in contrast to blocks, the fragments impart to the new polymer an insignificant proportion of the properties characteristic of their high-molecular-weight homologue.

Bearing in mind the foregoing considerations, the hierarchy of linear copolymers can be represented as follows as a function of the length of the sequences of elementary units incorporated in the macromolecule:



Here a is the elementary unit and f, s, x, and y are the numbers of elementary units ($f < s$ and $x \leqslant y$).

Taking into account the fact that the block length should not be smaller than the length of the segment, the structure of block copolymers can be described by terms such as segment-monomeric, segment-fragmental, segment(1)–segment(2)-al, etc. copolymers (Table 1). These names enumerate initially the polymeric segments with structures (1), (2), etc. in the copolymer macromolecule and indicate the nature of the chain-lengthening agent (if one is used), whereby the segments are chemically combined in the macromolecule.

We shall examine the definitions of certain characteristics of the block copolymers presented in Table 1. A component is a block of a homopolymer or a copolymer having a definite composition and structure incorporated in the block copolymer. "Componentality" is the number of blocks of different composition and structure constituting the macromolecules of the block copolymer. One-component block copolymers contain blocks of a single chemical kind connected via the residues of the chain-lengthening agent; the molecules of two-component block copolymers include blocks with two different structures, which may differ by the presence of other substituents or by the steric structure of the chain, etc. The type composition of a block copolymer (it can be a one-type, two-type, three-type, and multitype copolymer) is a quantity equal to the number of types of macromolecular compounds incorporated in the form of chemically combined oligomeric analogues (blocks) in the macromolecule of the block copolymer. "Blockability" is the total number of blocks of any kind in the macromolecule of the block copolymer. The minimum number of blocks which can be observed in long-block copolymers is two and the maximum number is determined by the length of the constituent blocks and the length of the macromolecule of the block copolymer itself and can amount to several tens. In terms of the regularity of the alternation of blocks along the macrochain, block copolymers of the polycondensation type can be divided into regularly alternating and irregularly alternating. This characteristic of block copolymers refers to their fine structure (microstructure) and its determination, particularly for irregularly alternating block copolymers, is as yet difficult.

Table 1. Characteristics of block copolymers.

Structure of copolymer	No. of components ('componentality')	No. of blocks ('blockality')	No. of types	Regularity in alternation of blocks
Segment-monomeric	1	two-, three-, and multi-block	1	regularly and irregularly alternating
Segment-fragmental	1	two-, three-, and multi-block	1	ditto
Segment-fragment-monomeric	1	three- and multi-block	1	ditto
Segment (1)-segment(2)-al	2	two-, three-, and multi-block	1 and 2	regularly alternating
Segment(1)-segment(2)-monomeric	2	two-, three- and multi-block	1 and 2	regularly and irregularly alternating
Segment(1)-segment(2)-fragmental	2	two-, three-, and multi-block	1 and 2	ditto
Segment(1)-segment(2)-segment(3)-al	3	three- and multi-block	1,2 and 3	ditto
Segment(1)-segment(2)-segment(3)-monomeric, etc.	3 (multi-component)	three- and multi-block > 3 (multiblock)	1,2 and 3 ⩾ 1	ditto

The chemical structure of polymers can be treated at two different levels: at the levels of the macrostructure and the microstructure. The macrostructure of the polymer is characterised by parameters of the following kind:

I. The chemical structure of the elementary unit of the polymer (idealised formula which does not reflect all the characteristics of the polymer chain structure).

II. The average chemical (elemental) composition of the polymer.

III. The average molecular weight of the polymer. The knowledge of the macrostructure of the polymer is usually sufficient to achieve a comparative characterisation of different polymers, but the macrostructure cannot explain the whole series of features of the physical and chemical properties of high-molecular-weight compounds. In such instances a more detailed study of polymers, yielding information about their microstructure, is necessary.

The concept of the microstructure of the polymer is much more profound than the concept of its macrostructure and includes a much greater number of parameters characterising the structure of the polymeric compound [16-20]; these parameters are listed below:

I. The chemical structures of the main and "anomalous" [18,19] elementary units in the chain (the heterounit property of polymers), terminal blocks, units, and terminal functional groups.

II. Chemical inhomogeneity:

1. Inhomogeneity with respect to molecular weight.

2. Inhomogeneity with respect to chemical composition (compositions inhomogeneity).

3. Inhomogeneity with respect to chemical structure [18, 19]: (a) inhomogeneity with respect to the degree of branching (number of branching points, chemical structure, and length of branches); (b) inhomogeneity in the "head-to-head" and "head-to-tail" combinations of units; (c) inhomogeneity as regards the presence of isomeric units; (d) inhomogeneity with respect to microtacticity (owing to the differences in the configurations of the asymmetric carbon atoms making up the macromolecular chain); (e) inhomogeneity of macromolecules induced by the presence of anomalous units owing to incomplete trimerisation, incomplete formation of the carbo- or hetero-cycle in the polycyclisation or polycyclocondensation reaction, copolymerisation and copolycondensation, and chemical reactions of the units in the macromolecules.

4. Inhomogeneity with respect to the chemical nature of the terminal blocks, units, and functional groups.

III. Inhomogeneity in the distribution of the main and anomalous units and sections of different chemical compositional structure in the macrochain.

One should note that, whereas the method for the determination of the macrostructure of the polymer has now been thoroughly developed and presents no difficulty, the determination of its microstructure is difficult even for simple polymeric systems. This problem becomes still more complex on passing from homopolymers to copolymers and block copolymers [17,20].

Nevertheless, even without experimental data for the microstructure of block copolymers of the polycondensation type, one can assume that these block copolymers will exhibit an appreciable inhomogeneity, i.e. a difference between the macromolecules of the same specimen of the block copolymer.

We shall now consider in a general form certain kinds of block copolymers of the polycondensation type and methods for their synthesis.

A. ONE-COMPONENT BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

One-component block copolymers are at the same time one-type block copolymers and can have a two-, three-, and multi-block structure (Table 1). One-component two-block copolymers can be obtained by the interaction of an excess of the oligomer having terminal functional groups f with a monomeric or fragmental chain lengthening agent (cl):

$$2\ \mathrm{f{-}A{-}f} + \mathrm{f'{-}cl{-}f'} \rightarrow \mathrm{f{-}A{-}cl{-}A{-}f}\ . \qquad (1)$$

One-component three-block copolymers can also be obtained from the same initial compounds as two-block copolymers, but in this case two stages are required; the low-molecular-weight compound can behave under these conditions as a functional group substituting agent (fgs) (monomeric or fragmental) in the oligomer rather than a chain lengthening agent:

$$\mathrm{f{-}A{-}f} + 2\mathrm{f'{-}fgs{-}f'} \xrightarrow{(a)} \mathrm{f'{-}fgs{-}A{-}fgs{-}f'}\ ;$$
$$\mathrm{f'{-}fgs{-}A{-}fgs{-}f'} + 2\mathrm{f{-}A{-}f} \xrightarrow{(b)} \mathrm{f{-}A{-}fgs{-}A{-}fgs{-}A{-}f}\ . \qquad (2)$$

Thus the functional group substituting agent is a low-molecular-weight compound used to substitute one set of functional groups in oligomers and polymers by another, whereby block copolymers having a specified structure can be synthesised. Functional group substituting agents can be divided into those whose residues are incorporated in the macromolecule of the block copolymer (monomeric and fragmental substituting agents) and substituting agents which are not incorporated in the macromolecule of the block copolymer (H_2O, $POCl_3$, etc.).

One-component multiblock copolymers are formed when equimolar amounts of a bifunctional oligomer react with a single chain lengthening agent:

$$n\,\mathrm{f{-}A{-}f} + n\,\mathrm{f'{-}cl{-}f'} \rightarrow \mathrm{f{-}[{-}A{-}cl{-}]_n{-}f'} \qquad (3)$$

or simultaneously with several chain lengthening agents of different chemical types. In the latter case one may speak of a regular or irregular alternation of lengthening agents of different kinds along the macrochain of the block copolymer.

Before the synthesis of a multiblock block copolymer, the initial oligomers may be subjected to interaction with a rigorously stoichiometric or an excess amount of functional group substituting agents in order to replace functional groups inactive with respect to the chosen chain lengthening agent by active groups:

$$n\,\mathrm{f''{-}A{-}f''} + 2n\,\mathrm{f{-}fgs{-}f} \xrightarrow{(a)} n\,\mathrm{f{-}fgs{-}A{-}fgs{-}f}\ ; \qquad (4)$$
$$n\,\mathrm{f{-}fgs{-}A{-}fgs{-}f} + n\,\mathrm{f'{-}cl{-}f'} \xrightarrow{(b)} \mathrm{f{-}[{-}fgs{-}A{-}fgs{-}cl{-}]_n{-}f'}\ .$$

Among one-component multiblock block copolymers, one can distinguish block copolymers with constant block lengths:

$$\sim\!\!\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\sim$$

and variable block lengths (varied, for example, by one of several chain lengthening agents, which do not yield an anomalous unit on combination of two oligomers):

$$\sim\!\!\overset{A}{\text{—}}\mathrm{cl}_2\overset{A(A+A+A)}{\text{———}}\mathrm{cl}_3\overset{A}{\text{—}}\mathrm{cl}_3\overset{A(A+A)}{\text{———}}\mathrm{cl}_2\overset{A}{\text{—}}\sim\ .$$

All the polymers containing anomalous units in their macromolecules can be regarded as the latter variety of block copolymers.

B. TWO-COMPONENT BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

Since most attention is being devoted nowadays to the synthesis and the study of the properties of block copolymers of this kind, we shall consider them in greater detail. Two-component two-block copolymers of type A–B may be obtained by the interaction of two polymers, each containing at the ends of its macrochains one functional group capable of polycondensation, and by the interaction of a stoichiometric amount of a chain lengthening agent with an equimolar amount of two polymers whose molecules each contain one functional group at the end of the chain:

$$\mathrm{A{-}f} + \mathrm{f'{-}cl{-}f'} + \mathrm{f{-}B} \rightarrow \mathrm{A{-}cl{-}B}\ . \qquad (5)$$

The polymers A–f and f–B, which differ in their composition or structure, may belong either to polymers of one type (a polyether, a polyamide, etc.) or to two different types of polymers (a polycarbonate and a polyorganosiloxane, a polyester and a polyether, etc.).

Two-component three-block block copolymers with A–B–A and B–A–B block sequences can be obtained by the interaction of a bifunctional oligomer B or A with an excess of the oligomer A or B respectively:

$$\geqslant 2f-A-f+f'-B-f' \rightarrow f-A-B-A-f \quad . \qquad (6)$$

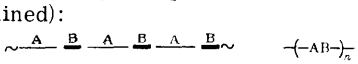
If one of the initial oligomers contains only one functional group at the end of the chain, the synthesis of the three-block copolymer is simplified:

$$2\,A-f+f'-B-f' \rightarrow A-B-A \quad . \qquad (7)$$

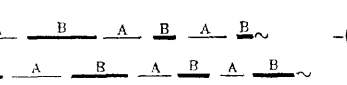
Two-component multiblock copolymers of the polycondensation type may be regularly alternating or irregularly alternating (regular and irregular).

1. Regularly Alternating Block Copolymers

Regularly alternating block copolymers are multiblock copolymers with a regular alternation of blocks of different kinds along the macrochain. Among the block copolymers of this kind, one should distinguish regularly alternating block copolymers with constant block lengths (within the limits of the polydispersity with which the initial oligomers having the specified molecular weight have been obtained):



and regularly alternating block copolymers with varying block lengths (one or both):



In view of the different types of behaviour under certain conditions of blocks of the same kind but different lengths, the block copolymers $-(-AB-)_n-$, $-(-A'B-)_n-$, $-(-AB'-)_n-$, and $-(-A'B'-)_n-$ will apparently exhibit different properties.

Regularly alternating two-component multiblock copolymers can be obtained in one stage when the initial oligomers have terminal functional groups of different types which interact with one another:

$$\begin{aligned} &3n\,f-A-f+3n\,f'-B-f' \rightarrow f'-B-(-A-B-)_n-f'+\\ &+f-(-A-B-)_n-A-f+f'-B-(-A-B-)_{n-2}-A-f \quad . \end{aligned} \qquad (8)$$

On the other hand, if the initial oligomers have terminal functional groups of the same type which do not interact with one another, regularly alternating block copolymers are formed in two stages and it is necessary to use a functional group substituting agent. Compared with the previous case, a wider spectrum of different block copolymer macromolecules is formed, the copolymers differing from one another in the nature of the terminal blocks, units, and functional groups:

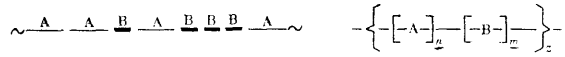
$$\begin{aligned} &10n\,f-A-f+20n\,f'-fgs-f' \xrightarrow{(a)} 10n\,f'-fgs-A-fgs-f' \xrightarrow{(b)}\\ &\xrightarrow{+10n\,f-B-f} f-B-(-fgs-A-fgs-B-)_n-f+\\ &+f-(-A-fgs-B-fgs-)_n-A-f+f-B-(-fgs-A-fgs-B-)_{n-2}-\\ &-fgs-A-f+f'-fgs-B-(-fgs-A-fgs-B-)_n-f+\\ &+f'-fgs-B-(-fgs-A-fgs-B-)_n-fgs-f'+ \end{aligned} \qquad (9)$$

$$\begin{aligned} &+f'-fgs-(-A-fgs-B-fgs-)_n-A-f+\\ &+f'-fgs-(-A-fgs-B-fgs-)_n-A-fgs-f'+\\ &+f'-fgs-B-(-fgs-A-fgs-B-)_{n-2}-fgs-A-f+\\ &+f-B-(-fgs-A-fgs-B-)_{n-1}-fgs-A-fgs-f'+\\ &+f'-fgs-B-(-fgs-A-fgs-B-)_{n-2}-fgs-A-f \end{aligned}$$

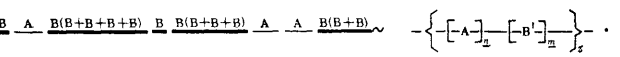
Thus the macromolecules of two-component regularly alternating multiblock copolymers of the polycondensation type differ from one another by the molecular weight of both the macromolecules themselves and their constituent blocks, by their chemical composition and structure, by the inhomogeneity in the distribution of the main and anomalous units along the chain (blocks and the macromolecules), and by the nature of the terminal blocks, units, and functional groups.

2. Irregularly Alternating Block Copolymers

Irregularly alternating block copolymers are multiblock copolymers with an irregular alternation of blocks of different kinds. Among block copolymers of this type, one should distinguish irregularly alternating block copolymers with constant block lengths (within the limits of the polydispersity with which the original oligomers having a specified molecular weight have been obtained):



and irregularly alternating block copolymers with varying (for example on increasing the length of block B without the appearance of an anomalous unit) lengths of the blocks (one or both):



(The subscripts $\underline{n}$ and $\underline{m}$ denote an irregular distribution of blocks A and B along the macrochain.)

Many methods for the synthesis of irregularly alternating two-component block copolymers have now been described; an even greater number appear to be possible in view of the prospects arising from the very principle of the synthesis of these block copolymers. We may formulate these methods of synthesis in an abbreviated form (each component is an individual substance):

ol + m + cl,	ol-1 + ol-2,
ol + m-cl,	ol-1 + ol-2 + cl,
ol + cm + cm-cl,	cm-1 + cm-2,
ol + cm-fgs + cm-cl,	

where ol is a bifunctional oligomer, m a monomer (a substance capable of homopolycondensation), m-cl a substance behaving simultaneously as a monomer and a chain lengthening agent, cm a comonomer (a substance incapable of homopolycondensation), cm-cl a substance behaving as a comonomer and a chain lengthening agent (for example, a diol in the synthesis of polyurethanes), and cm-fgs a substance behaving simultaneously as a monomer and a functional group substituting agent (for example, di-isocyanate in one of the methods for the synthesis of polyurethanes).

We shall now consider block copolymers obtained by two of the most frequently used methods for the synthesis of irregular block copolymers.

(a) Irregular (ol-1 + ol-2 + cl) two-component multiblock copolymers. Such block copolymers are formed when the initial oligomers with

terminal groups of the same type which do not interact with one another are combined into a common macrochain in a single stage with the aid of a chain lengthening agent:

$$\begin{aligned} &zn\,f{-}A{-}f + zm\,f{-}B{-}f + z(n+m)\,f'{-}cl\ {-}f' \rightarrow \\ &\rightarrow f{-}A{-}cl\ {-}\{{-}[{-}A{-}cl\ {-}]_{\underline{n}}{-}[{-}B{-}cl\ {-}]_{\underline{m}}{-}\}_z{-}A{-}f + \\ &+ f'{-}cl\ {-}A{-}cl\ {-}\{{-}[{-}A{-}cl{-}]_{\underline{n}}{-}[{-}B{-}cl{-}]_{\underline{m}}{-}\}_z{-}A{-}cl{-}f' + \\ &+ f'{-}cl\ {-}A{-}cl\ {-}\{{-}[{-}A{-}cl\ {-}]_{\underline{n}}{-}[{-}B{-}cl\ {-}]_{\underline{m}}{-}\}_z{-}A{-}f + \text{etc.} \end{aligned} \quad (10)$$

In all, there is a possibility of ten combinations of terminal blocks, units, and functional groups:

A ~ A; cl–A ~ A–cl; cl–A ~ A;
B ~ B; cl–A ~ B–cl; cl–B ~ B;
A ~ B; cl–A ~ B–cl; cl–A ~ B; A ~ B–cl.

The macromolecules of irregular (ol-1 + ol-2 + cl) two-component multiblock copolymers of the polycondensation type differ from one another by the molecular weights of both the macromolecules themselves and their constituent blocks, by the chemical composition (determined mainly by the molecular weight and numbers of blocks of different kinds) and chemical structure, by the inhomogeneity in the distribution of the main and anomalous units along the chain (blocks and macromolecules), by the inhomogeneity in the distribution of blocks of different chemical composition or structure along the macrochain, and by the nature of terminal blocks, units, and functional groups [Eqn.(10)].

The examples quoted show that the chain lengthening agent is a low-molecular-weight compound (monomeric or fragmental) which is capable of reacting with oligomers or low-molecular-weight polymers having terminal functional groups and thereby lengthening the polymer chain. Furthermore, compounds which interact simultaneously with the initial oligomer and with the low-molecular-weight compound, intended for the synthesis of a non-oligomeric block, also behave as chain lengthening agents. Depending on the chemical structure of the initial oligomer, the chain lengthening agent can be of the same kind (its residue is present in the oligomer chain) or "alien" in relation to the oligomer (the oligomer does not contain residues of this kind). If the chain lengthening agent is used to synthesise at least one of the initial oligomers, then the molecular weight of blocks of different chemical composition or structure is related not only to the numbers of blocks A or B in a single macrochain but also to their length, which may differ from the length of the initial oligomers (an irregularly alternating block copolymer with varying block lengths). If the chain lengthening agent is of an "alien" type, then the overall molecular weight of blocks of the same kind will be determined by their number in the macromolecule.

The number of blocks A and B in the macrochain is a statistical quantity and depends on the length of the entire macrochain, on the conditions for the synthesis of the block copolymer, on the relative reactivities of the terminal functional groups of the oligomers, and on the nature of the chain lengthening agent. Precisely in the case of a homogeneous chain lengthening agent the number of the corresponding (related) blocks, for example A, may be greatly reduced owing to the increase in their length without the appearance of heterounits. In the case of an "alien" chain lengthening agent, each block of the macrochain, including blocks of the same nature, is separated from others by an anomalous unit. In this situation the number of blocks A or B in a single macrochain is therefore determined by the number of oligomers f–A–f or f–B–f used to form the macrochain.

(b) Irregular (ol + cm + cm-cl) two-component multiblock copolymers. Such block copolymers are formed in a single stage from the initial oligomer, for example, f–B–f, and the monomer f–A–f or f″–A–f″ with the same functional groups as in the oligomer or others which are also capable of reacting with a chain lengthening agent:

$$\begin{aligned} &zn\,f{-}a{-}f + zm\,f{-}B{-}f + z(n+m)\,f'{-}cl{-}f' \rightarrow \\ &\rightarrow f{-}\{{-}[{-}a{-}cl{-}]_{\underline{n}}{-}[{-}B{-}cl{-}]_{\underline{m}}{-}\}_z{-}a{-}f + \\ &+ f'{-}cl\ {-}\{{-}[{-}a{-}cl{-}]_{\underline{n}}{-}[{-}B{-}cl{-}]_{\underline{m}}{-}\}_z{-}a{-}cl\ {-}f' + \\ &+ f{-}\{{-}[{-}a{-}cl{-}]_{\underline{n}}{-}[{-}B{-}cl\ {-}]_{\underline{m}}{-}\}_z{-}a{-}cl{-}f' + \text{etc.}; \end{aligned} \quad (11)$$

In all, there is a possibility of 21 combinations of terminal blocks, units, and functional groups.

In this case [Eqn.(11)] the molecular weight of blocks A = $-(-a-cl-)_n-$ in individual macromolecules is determined not only by the number of these blocks but also by their length. Variations in the length of blocks A in irregular (ol + cm + cm-cl) block copolymers may be more numerous than in the case of irregular (ol-1 + ol-2 + cl) block copolymers.

The considerations described in relation to two-component block copolymers show that the determination of the complete microstructure of block copolymers of the polycondensation type constitutes an extremely complex and important problem, which still awaits solution. In the present stage the determination of the microstructure of polymers is frequently limited to the determination of the molecular weight distribution and the distribution with respect to chemical composition.

C. THREE-COMPONENT BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

It is possible to distinguish the following kinds of such block copolymers:

1. Three-component three-block copolymers in which the distribution of blocks of different chemical kinds along the macrochain is of the type A–B–C, A–C–B, or B–A–C.

2. Three-component multiblock copolymers. These block copolymers can be regularly alternating, $-[-A-B-C-]_z-$, $-[-A-C-B-]_z-$, and $-[-B-A-C]_z-$, or irregularly alternating, $-\{-[A-]_n--[-B-]_m--[-C-]_p--\}_z-$, etc. with constant or variable block lengths.

The properties of three-component block copolymers can be greatly influenced by the distribution of different blocks along the copolymer macrochain. Depending on the chemical nature of the constituent blocks and the required structure of the final polymeric product, three-component multiblock copolymers can be synthesised in one or two stages from mono- or bi-functional oligomers and may require the use of different chain lengthening agents and functional group substituting agents. Two-, three-, and multi-block seeds with terminal functional groups can also be used as the initial compounds.

D. MULTICOMPONENT BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

It is possible to distinguish the following kinds of such block copolymers:

1. Multicomponent block copolymers in which the number of blocks in the chain is equal to the number of

components or slightly exceeds it, for example, four-component four-block A–B–C–D copolymers, five-component six-block A–B–C–D–E–A copolymers, etc. These block copolymers can have a large number of analogues differing from one another by the distribution of blocks of different chemical types along the macrochain.

2. Multicomponent multiblock copolymers which can be regularly alternating with constant or variable block lengths, $-[-A-B-C-D-E-]_z-$, etc., or irregularly alternating with constant or variable block lengths, namely $-\{-[-A-]_{\underline{n}}-[-B-]_{\underline{m}}-[-C-]_{\underline{p}}-[-D-]_q-\}_z-$, etc.

III. ONE-TYPE BLOCK COPOLYMERS

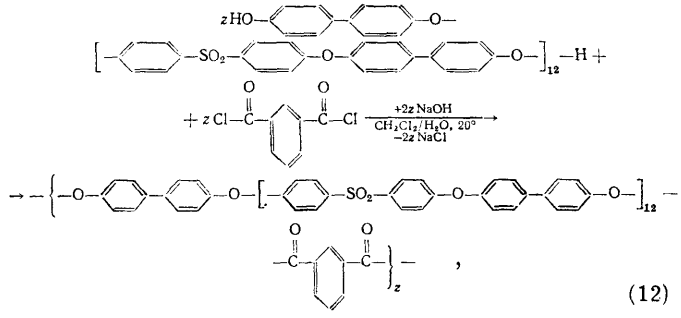
One-type block copolymers of the polycondensation type are copolymers consisting of polymer blocks of the same type which have identical or different compositions. Such block copolymers can be synthesised for the following purposes: (a) to increase the molecular weight of low-molecular-weight polymers having one or two terminal functional groups; (b) to obtain polymers with a uniform distribution of functional groups along the chain; (c) to modify the properties of the polymer by means of residues of the chain lengthening agent (monomeric or fragmental); (d) to modify the properties of the polymer by introducing into its macromolecules blocks of a polymer-analogue differing in its properties.

The increase in the molecular weight of polymers with the aid of a chain lengthening agent may be important in many instances, since many processes yielded only low-molecular-weight polymers are known. In particular, the molecular weight of poly(phenylene oxide) based on 2,6-dimethylphenol may be increased by a factor of two when its sodium salt interacts with di-(4-chlorophenyl) sulphone[23]. The two-block copolymer formed as a result made it possible to obtain stable relatively flexible films.

The low molecular weight of polymers with a system of conjugated multiple bonds greatly impairs their physicomechanical properties and reduces the possibility of obtaining polymeric materials on their basis. The lengthening of the molecules of such low-molecular-weight polymers by means of chain lengthening agents, for example, the poly-Schiff base derived from *p*-phenylenediamine and benzil using a di-isocyanate or a dicarboxylic acid[24], lead, according to Eqn.(1), to the formation of multiblock copolymers with improved physicomechanical properties and effective semiconducting properties.

Block copolymers obtained from oligomers and trifunctional chain lengthening agents (two groups out of three being of the same kind) may be of interest as polymers capable of forming structures with a specified density of the chemical network and also as initial polymers for the synthesis of graft copolymers having a specified frequency of branching points.

The modification of the properties of polymers by the introduction of the residues of a monomeric or fragmental chain lengthening agent, for example, by the interaction of bifunctional oligomers with a chain lengthening agent [Eqn.(1)], is attractive in view of its simplicity: for any bifunctional oligomer intended for subsequent synthesis of two-type block copolymers, it is possible to select a whole series of readily available chain lengthening agents. For example, dihydroxyoligo(arylene sulphone oxides) can react with aromatic[25] and aliphatic[26] dicarboxylic acid dichlorides:



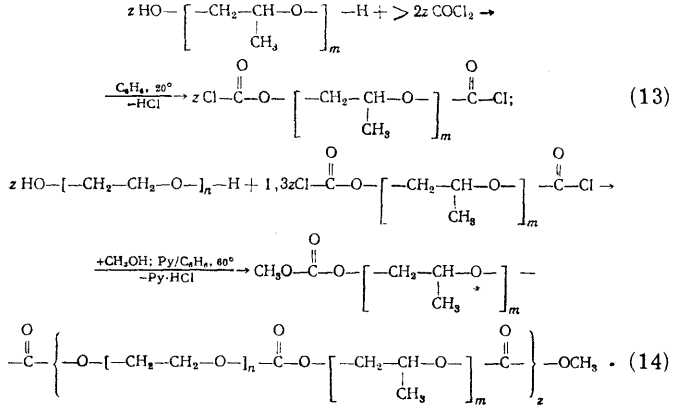
(12)

and with aromatic disulphonyl chlorides[25]. The block copolymers obtained exhibit a high thermal and hydrolytic stability and have useful mechanical and dielectric properties. Segmental-monomeric block copolymers with improved mechanical properties have been obtained from low-molecular-weight polycarbonates having terminal chloroformate groups and diamines, for example, piperazine[27]. Modified polyquinazolinones with improved thermal properties and ready solubility in many solvents have been obtained by the interaction of oligoquinazolinones with terminal amino-groups and pyromellitic dianhydride[28].

In all the examples quoted above one-component block copolymers were described, but the synthesis of two-component one-type block copolymers for which one may expect interesting combinations of the properties of polymer-analogues are of no less interest.

1. Polyether–Polyether Block Copolymers

Regularly alternating multiblock poly(ethylene oxide)-poly(propylene oxide) block copolymers have been obtained[29], in conformity with Eqn.(4), by the condensation of α,ω-dihydroxypoly(ethylene oxide) with poly(propylene oxide) α,ω-bischloroformate. The chloroformate derivative of α,ω-dihydroxypoly(propylene oxide) was obtained with the aid of phosgene, which behaves in this instance as a functional group substituting agent:



(13)

(14)

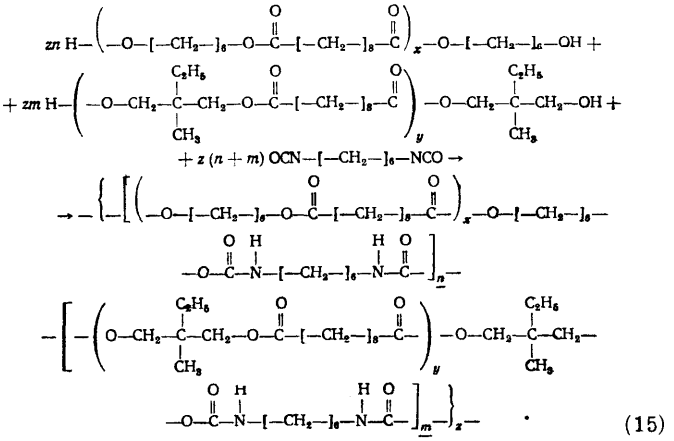
In the resulting block copolymers the crystalline lamellar phase consists of poly(ethylene oxide) blocks and the amorphous phase is made up of poly(propylene oxide) blocks. According to dilatometric data, the degree of

crystallinity of multiblock copolymers is lower by 60% than the degree of crystallinity of the corresponding three-block copolymers. The crystallinity of the specimens increased when the latter were annealed; the melting points of the block copolymers ranged from 37° to 56°C depending on composition [29].

Irregular (ol + m-Cl) multiblock poly(2,6-dimethylphenylene oxide)-poly(2,6-diphenylene oxide) block copolymers have been obtained by the dehydropolycondensation of 2,6-dimethylphenyl in the presence of oligo-(2,6-diphenylphenylene oxide) [30]. Oxidation of a mixture of 2,6-dimethylphenol with 2,6-diphenylphenol leads to the formation of a statistical copolymer; oxidation of 2,6-diphenylphenol in the presence of poly-(2,6-dimethylphenylene oxide) prepared beforehand leads to a mixture of part of the initial polymer and of the newly formed statistical copolymer as a result of exchange processes occurring in the course of dehydropolycondensation. Depending on the method of isolation of the block copolymer from the reaction mixture, the oligo-(2,6-dimethylphenylene oxide) blocks can constitute the amorphous or crystalline phase. The oligo-(2,6-dimethylphenylene oxide) blocks in the isolated copolymer always constitute the amorphous phase, but they crystallise on heating, while oligo(2,6-diphenyl oxide) blocks become amorphous. The block copolymers synthesised are inhomogeneous with respect to chemical composition: on heating their solutions in *m*-xylene, macromolecules enriched in oligo-(2,6-diphenylphenylene oxide) blocks are precipitated.

2. Polyester–Polyester Block Copolymers

There are numerous examples of the synthesis of two-component block copolymers the constituent block of which consists of polyesters. In particular, the reaction of a mixture of two hydroxylated or carboxylated low-molecular-weight aliphatic [poly(ethylene sebacate), poly-(ethylene succinate), poly(ethylene adipate) and poly-(propylene adipate) [31], poly(butylene saccinate) and poly(butylene sebacate) [32], poly(hexamethylene sebacate) and poly-(2-ethyl-2-methyl-1,3-propylene sebacate) [33] or aromatic and aliphatic [poly(ethylene terephthalate) and poly(ethylene succinate) poly(ethylene adipate), etc. [34]] polyesters with di-isocyanates yielded irregular (ol-1 + ol-2 + cl) block polymers:



(15)

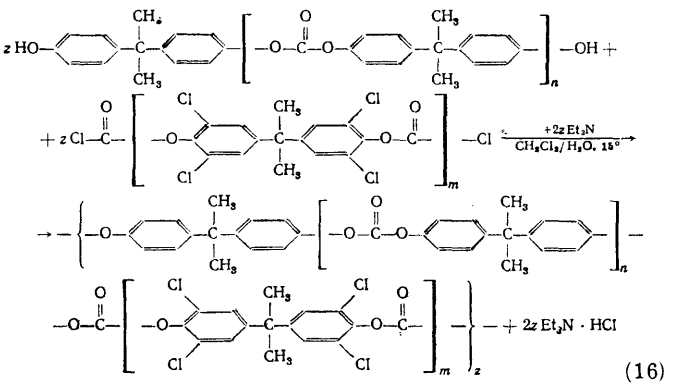
Multiblock poly(hexamethylene sebacate)–poly(2-ethyl-2-methyl-1,3-propylene sebacate) block copolymers [see Eqn.(15)] contain blocks consisting of isomeric polymers having identical chemical compositions but different chemical structures: the first polymer is highly crystalline with $T_m = -70°C$, while the second is entirely amorphous; its $T_g = -69°C$. [33] These block copolymers contain crystalline and amorphous phases and, as the content of crystallising oligo-(hexamethylene sebacate) blocks in the block copolymer increases, i.e. as the number of these blocks in the macrochain diminishes, the degree of crystallinity of the block copolymers increases. It has been suggested that [35] this is associated with the marked dependence of the crystallinity of the blocks on their molecular weight, i.e. on the fact that an isolated block as it were recovers its initial length, whereupon its ability to crystallise and undergo aggregation with other crystallising blocks of the same type becomes more marked. Dielectric relaxation studies on specimens have shown that β-relaxation processes in block copolymers depend on their composition and are associated with the relaxation of the polymethylene chain fragments [36].

Irregular (ol + cm + cm-cl) polyester–polyester block copolymers have been obtained from oligo(butylene adipate) with terminal hydroxy-groups, butylene glycol, and dimethyl terephthalate [37]. These block copolymers manifest the properties of thermoelastoplastic materials.

Regularly alternating poly(decamethylene terephthalate)–poly(decamethylene isophthalate) block copolymers have been obtained by the reaction of previously formed oligomers, one of which contained hydroxy-groups and the other contained acid chloride functional groups [38]. The same method has been used to synthesis other similar block copolymers.

3. Polycarbonate–Polycarbonate Block Copolymers

A typical method for the synthesis of these block copolymers involves the interaction of two reaction solutions containing oligocarbonates with hydroxy- or chloroformyl terminal functional groups synthesised by interfacial polycondensation from various bisphenols [29]



(16)

The thermalstabilities of polycarbonate–polycarbonate block copolymers are superior to those of statistical copolymers having an analogous composition. Some of them have been recommended as a base for photographic materials.

Polycarbonate–polycarbonate block copolymers can also be obtained by other synthetic procedures, for example, by the introduction of measured amounts of starting materials into the reaction medium, by the interaction of a mixture of an oligocarbonate prepared beforehand and a bisphenol with phosgene to give irregular (ol + cm + cm-cl) block copolymers, etc.

4. Polysulphide–Polysulphide Block Copolymers

Irregular (ol-1 + ol-2) aliphatic multiblock polysulphide–polysulphide block copolymers can be obtained by oxidising a mixture of two or more liquid (M.W. = 4000 to 8000) oligosulphides of various structure having terminal mercapto-groups[40]. Such block copolymers possess unique physicomechanical properties at low temperatures.

5. Polyamide–Polyamide Block Copolymers

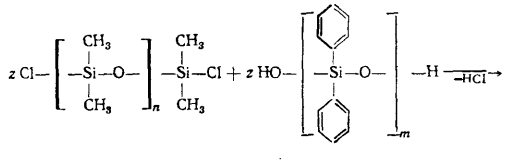
Polyamide–polyamide block copolymers of the polycondensation type can be obtained by a number of procedures, particularly by the polycondensation in the melt of a mixture of primary and secondary aliphatic–aromatic diamines, having appreciably different reactivities, with aliphatic dicarboxylic acids[41]. These crystallising irregular (cm-1 + cm-2 + cm-3) block copolymers consist of two phases and have two melting points.

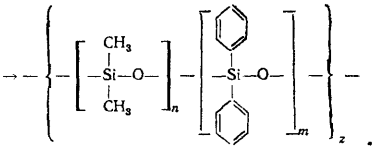
Irregular (ol-1 + ol-2 + cl) block copolymers have been obtained by the interaction of two diamino-oligoamides of different structure with di-isocyanates[42]. Two-component block copolymers with a regular alternation of polyamide blocks have been obtained by the interaction of diamino- and dichloroformyl-oligoamides synthesised from *trans*-2,5-dimethylpiperazine and the dichlorides of dicarboxylic acids such as terephthalic, isophthalic, and sebacic acids[43,44] and from *p*-diaminobiphenyl or *trans*-2,5-dimethylpiperazine and terephthalic or adipic acid dichloride[45,46].

6. Polyorganosiloxane–Polyorganosiloxane Block Copolymers

Block copolymers consisting of polyorganosiloxane blocks can be obtained in different ways; in particular, multiblock regularly alternating polydimethylsiloxane–polydiphenylsiloxane block copolymers of the polycondensation type have been obtained by the interaction of "living" block copolymers of the polymerisation type with a chain lengthening agent[47]. The initial four-block copolymer B–A–A–B was obtained by the polymerisation of hexamethylcyclotrisiloxane in the presence of an initiator (a complex of the dilithium salt of 1,1,3,3-tetraphenyldisiloxanediol with hexamethylphosphoramide) with subsequent addition and polymerisation of hexaphenylcyclotrisiloxane. When structured polydimethylsiloxane–polydiphenylsiloxane block copolymers are compared, the best properties are exhibited by multiblock copolymers. Both types of block copolymers have analogous morphologies, but the rate of formation of domains is higher for the multiblock copolymer. The continuous amorphous phase consists of polydimethylsiloxane and the dispersed phase consists of crystalline polydiphenylsiloxane domains[48].

Regularly alternating block copolymers can be obtained also by the heterofunctional condensation of oligosiloxanes, for example by the reaction of α,ω-dichloropolydimethylsiloxane with α,ω-dihydroxypolydiphenylsiloxane[49]:





(17)

They can also be synthesised by the reaction of polydiorganosiloxanediols with siloxane oligomers having terminal acetoxy-groups[50], alkoxy-groups, or hydrogen atoms.

Irregular (ol-1 + ol-2) polyorganosiloxane–polyorganosiloxane block copolymers can be obtained by the reaction (in the presence of catalysts) of two oligo-organosiloxanediols[49] or a mixture of two oligodiols and a silanol[51]. Readily structured irregular (ol + m-1-cl + m-2-cl) block copolymers can be obtained from oligo-organosiloxanediol, trichlorophenylsilane, and dichloromethylphenylsilane[52].

IV. TWO-TYPE BLOCK COPOLYMERS

Two-type block copolymers consist of polymer blocks belonging to two different types. Such block copolymers constitute the vast majority among block copolymers of the polycondensation type known hitherto. Two-type block copolymers may be synthesised for the following purposes: (a) for imparting elasticity to rigid-chain polymers; (b) for increasing the strength characteristics of elastomers; (c) for imparting hydrophilic properties to polymers; (d) for increasing the permeability of polymers to gases and the selectivity of their permeability; (e) for reducing the viscosity of melts of rigid-chain polymers; (f) for imparting antistatic properties to polymers; (g) for increasing the chemical stability of polymers; (h) for synthesising polymers capable of being degraded biologically, etc.

In order to achieve these aims, blocks of different polymers, having a wide variety of physicochemical properties, are combined in a single macromolecule. At the same time, whatever the properties of the constituent blocks of the block copolymers, they can be divided into (a) blocks with enhanced chain mobility (flexible blocks with a low thermal stability) and (b) blocks with a reduced chain mobility (rigid blocks with a high thermal stability). All two-type block copolymers can therefore be divided into the following groups:

A. Elastoplastic block copolymers (copolymers containing blocks with appreciably different thermal stabilities).

B. Thermoplastic block copolymers (copolymers containing blocks with relatively similar high thermal stabilities).

C. Elastomeric block copolymers (copolymers containing blocks with relatively similar low thermal stabilities).

A general list of block copolymers belonging to a particular group is presented in Table 2.

A. ELASTOPLASTIC BLOCK COPOLYMERS

1. Block Copolymers Containing Blocks Comprising Aliphatic Polyethers

Aliphatic polyethers are elastic crystallisable polymers. The presence of polar groups and the high flexibility of the macromolecules ensure a high solubility of the polymers in organic solvents. Poly(ethylene oxide) exhibits a

unique solubility in water. Some of the first block copolymers based on aliphatic polyethers were segmented polyurethanes incorporating polyurethane and polyurea block copolymers[1].

Table 2. Two-type block copolymers.

A. Elastoplastic block copolymers

Flexible block A	Rigid block B	References
Aliphatic polyether	Polyurethane*	14-17, 54-57
ditto	Polyurea*	14-17, 54-57
"	Polyester:	
"	aliphatic-aromatic	58-84
"	aromatic	84-87
"	Polycarbonate	88-92
"	Poly(arylene sulphone oxide)	93
"	Polyamide	94-100
"	Polystyrene	101-103
"	Cellulose	110-112
Aliphatic polyester	Polyurethane*	54-56
ditto	Polyurea*	54-56
"	Polycarbonate	88,113-115
"	Polyamide	116-117
Polydiene	Polyurethane*	55,56,61
"	Polyurea*	55,56,61
"	Polyamide	119
"	Polyimide	120
Aliphatic polysulphide	Polyurethane	121
ditto	Polyimidothioether	122
Polyorganosiloxane	Polyurethane*	54
ditto	Polyurea	54
"	Polytetramethylenesilphenylene-siloxane	123-125
"	Polystyrene	126-129
"	Poly-α-methylstyrene	130
"	Polycarbonate**	131-140
"	Poly(arylene sulphone oxide)**	141-144
"	Aromatic polyether	145
"	Polyester:	
"	aliphatic-aromatic	146,147
"	aromatic	148-154
"	Polyamide	98,155
"	Polyimide	156

B. Thermoplastic Block Copolymers

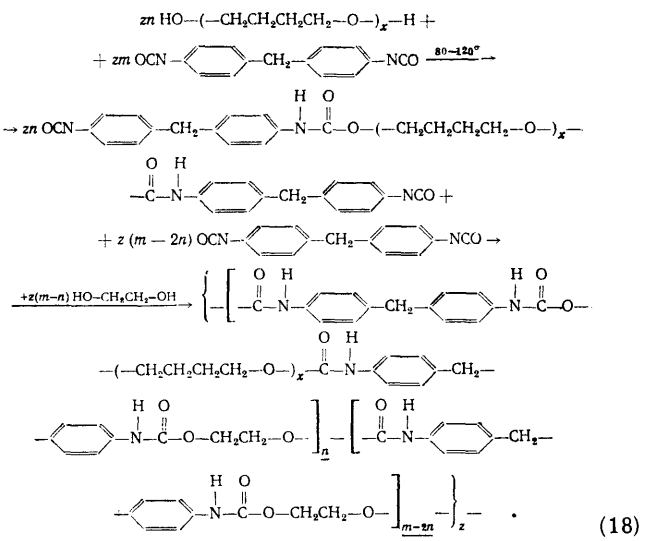
Rigid block A	Rigid block B	References
Polycarbonate	Polyurethane	157
ditto	Polystyrene	88,158
"	Poly(phenylene oxide)	159
"	Polyester (aliphatic-aromatic)	160
"	Poly(arylene sulphone oxide)	161,162
Poly(arylene sulphone oxide)	Polycarbonate	161,162
"	Polystyrene	8
"	Poly(phenylene oxide)	163
"	Polyester:	
"	aliphatic-aromatic	8
"	aromatic**	164,165
Polystyrene	Polycarbonate	88,158
ditto	Polyester	166
"	Poly(arylene sulphone oxide)	8
"	Polyamide	166
Polyether	Polycarbonate	159
ditto	Polyester	167
"	Poly(arylene sulphone oxide)	163
Polyester	Polycarbonate	160
ditto	Poly(arylene sulphone oxide)	8,164,165
"	Polystyrene	166
"	Polyether	167
"	Polyamide	168,169
Polyamide	Polystyrene	166
ditto	Polyester	168,169

C. Elastomeric Block Copolymers

Flexible block A	Flexible block B	References
Polydimethylsiloxane	Polyether*	7,170-172
ditto	Polyester	173

*Block copolymers manufactured on an industrial scale.
**Block copolymers manufactured in the form of experimental batches.

(a) Polyurethane–poly(alkylene oxide) block copolymers. Polyurethane–poly(alkylene oxide) block copolymers, which are some of the first block copolymers of the polycondensation type[53], consist of rigid polyurethane blocks (T_g† or T_m‡ in the range 100–250°C), obtained from a di-isocyanate and a low-molecular-weight glycol, and flexible poly(alkylene oxide) blocks ($T_g < 0$°C). Regularly alternating block copolymers are formed when equimolar amounts of oligo(urethane di-isocyanate) and oligo(alkene oxide)diol, obtained beforehand, are made to react. Irregular (ol + cm + cm-cl) copolymers are formed when all the starting materials are mixed simultaneously: the oligodiol, the low-molecular-weight glycol, and the di-isocyanate. However, irregular (ol + cm-fgs + cm-cl) urethane block copolymers, which are synthesised by a two-stage procedure, are nowadays of greatest importance, for example:



(18)

Oligoethers such as oligo(propylene oxide), oligo(tetramethylene oxide) etc. are used as the initial oligodiols with a molecular weight of 1000–3000 in the synthesis of polyurethane–poly(alkylene oxide) block copolymers; the initial di-isocyanates are methylenedi-(4-phenyl) di-isocyanate, tolylene di-isocyanate, 1,6-hexamethylene di-isocyanate, etc., and the initial low-molecular-weight glycols usually employed are 1,2-ethylene glycol, 1,4-tetramethylene glycol, etc.

Polyurethane–poly(alkylene oxide) block copolymers are microheterogeneous two-phase systems in which rigid oligourethane blocks, segregated into a separate phase owing to the incompatibility of the blocks, form 30–100 Å domains, greatly strengthened by strong intermolecular hydrogen bonds. Owing to the presence of a strong physical network, polyurethane block copolymers are very strong and hard and possess a high resistance to tearing and wear[14-17,54-57].

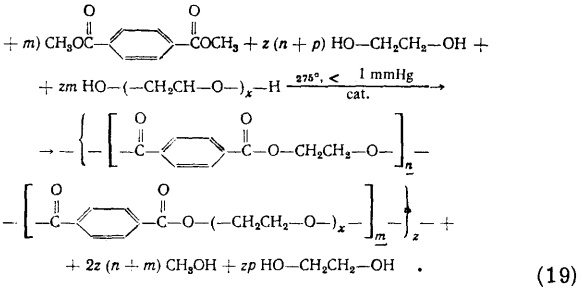
(b) Polyurea–poly(alkylene oxide) block copolymers. The principal difference between the synthesis of polyurethane–poly(alkylene oxide) and polyurea–poly(alkylene oxide) block copolymers involves the

† Glass point.

‡ Melting point.

use of diamines instead of glycols in the latter case. Owing to the presence of an excess of di-isocyanate [Eqn. (18)], the growth of rigid oligourea blocks is accompanied by the formation of a certain amount of biuret cross-links[55,56]. In contrast to polyurethane block copolymers, polyurea block copolymers are less stable in the melt but are harder. More detailed information about the synthesis and properties of polyurethane–poly(alkylene oxide) and polyurea–poly(alkylene oxide) block copolymers may be found in a number of reviews[14-17,54-57].

(c) Polyester–poly(alkylene oxide) block copolymers. Aliphaticaromatic or aromatic polyesters constitute the rigid blocks in block copolymers having this structure. Block copolymers containing rigid blocks of crystallising poly(ethylene terephthalate) (T_m = 265 °C) and flexible poly(ethylene oxide) blocks (T_m = 65 °C, T_g = −55 °C) as well as segmented polyurethanes were some of the first block copolymers of the polycondensation type synthesised[58-60]. Modification of poly(ethylene terephthalate) by replacing part of the ethylene glycol by oligo(ethylene oxide)diol with a molecular weight of 1000–6000 was undertaken in order to impart hydrophilic properties, an improved capacity for dyeing, and increased elasticity to poly(ethylene terephthalate) fibres. Irregular (ol + cm + cm-cl) poly(ethylene terephthalate)–poly(ethylene oxide) block copolymers, usually containing 20–30 wt.% of flexible blocks, are synthesised in the melt in the presence of a catalyst:

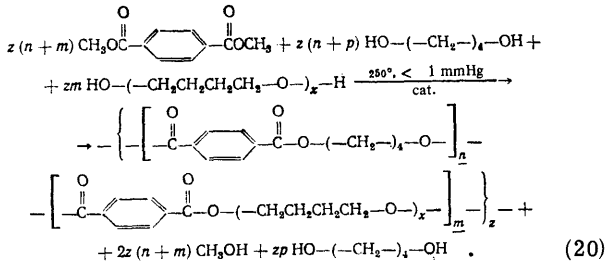


(19)

The disperse phase in the block copolymer is crystalline poly(ethylene terephthalate) and the continuous phase consists of amorphous poly(ethylene oxide) [oligo(ethylene oxide) blocks with a molecular weight of 1000–3000 remain amorphous, but, with increase of molecular weight to 6000, they may crystallise]. The poly(ethylene terephthalate) may be modified further by replacing part of the dimethyl terephthalate by dimethyl isophthalate[61] or by synthesising poly(ethylene terephthalate)–poly(tetramethylene oxide) block copolymers[62].

By analogy with poly(ethylene terephthalate)–poly(ethylene oxide) copolymers, it has been possible to synthesise in recent years poly(propylene terephthalate–poly(propylene oxide),[63] poly(tetramethylene terephthalate)–poly(propylene oxide),[64] poly(tetramethylene terephthalate)–poly(ethylene oxide),[65] poly(hexamethylene terephthalate)–poly(ethylene oxide),[66] and poly(alkylene terephthalate)–poly(tetramethylene oxide)[67] block copolymers. Among polymers of this type, the greatest interest attaches to poly(tetramethylene terephthalate)–poly(tetramethylene oxide) block copolymers, which are manufactured under the name Hytrel by the Du Pont Company.

Irregular (ol + cm + cm-ol) poly(tetramethylene terephthalate)–poly(tetramethylene oxide) block copolymers, initially intended for the synthesis of strong and elastic fibres[68], are synthesised in the melt in the presence of catalysts for equilibrium transesterification[69-71]:



(20)

The molecular weight of the initial oligo(tetramethylene oxide) (M.W. = 1000–4000) is usually 1000 and its content in the polymer is usually 30–70 wt.%.[70] In this composition range the block copolymer has in fact the most effective physicomechanical properties[70-82].

Owing to the presence of the crystalline phase, the block copolymers are insoluble in the majority of organic solvents. The rigid blocks in poly(tetramethylene terephthalate)–poly(tetramethylene oxide) copolymers crystallise very rapidly, so that there is no need for annealing articles made from this material, which cannot be said, for example, of poly(ethylene terephthalate)–poly(ethylene oxide) block copolymers, where the rate of crystallisation of rigid blocks is much lower[72]. The block copolymer containing 67% of the flexible blocks has T_m = 176 °C and T_g = −78 °C, the stress corresponding to 300% elongation is 110 kgf cm^{-2}, the tensile strength is 400 kgf cm^{-2}, and the relative elongation on rupture is 800%.

The block copolymers possess an unusual two-phase structure and consist of continuous (and not discrete) and interacting crystalline (in the form of lamellae) and amorphous domains[73].

Industrial brands of the Hytrel polymer contain a small amount of tetramethylene isophthalate units[70,82] and, depending on composition, have a tensile strength of 350 to 450 kgf cm^{-2} and a relative elongation on rupture of 500–600%. The block copolymers possess useful rheological properties and their melts have low viscosities and high stabilities and can be processed by rotational casting, casting under pressure, etc.[83] They are also distinguished by a high chemical stability, resistance to repeated deformation, and resistance to tearing, wear, and creep.

Irregular (ol + cm + cm-cl) block copolymers containing rigid aromatic polyester blocks (polyarylates) and flexible poly(ethylene oxide) or poly(propylene oxide) blocks have been obtained by high-temperature polycondensation in solution by the interaction of a mixture of a bisphenol, terephthalic acid dichloride, and oligo(alkylene oxide) diols[84,85]. The block copolymers exhibited high thermal stability and a solubility in organic solvents higher than that of polyarylates, but the increase in their elasticity was insignificant. At the same time regularly alternating, polyarylate–poly(ethylene oxide) block copolymers, obtained under the conditions of low-temperature polycondensation in solution from oligo(ethylene oxide) bischloroformate (M.W. = 1000–2000) and oligoarylate diol based on 2,2-di(4-hydroxyphenyl)propane and terephthalic acid dichloride, exhibit a high strength (100 to 350 kgf cm^{-2}) and a high relative elongation on rupture (700–400%) respectively. There are polyarylate and poly(alkylene oxide) crystalline and amorphous phases

respectively in these polymers and on extension the specimens are strengthened[86].

Regularly alternating polyarylate–poly(ethylene oxide) block copolymers containing blocks of amorphous polyarylate based on phenolphthalein and terephthalic acid dichloride (1000–5000) and poly(ethylene oxide) blocks (400–20 000) have been obtained under the conditions of acceptor-catalytic polycondensation from dihydroxyoligoarylates and dihydroxyoligo(ethylene oxides)[87]. Terephthalic acid dichloride and not phosgene[86] was used as the functional group substituting agent. When the molecular weights of the oligo(ethylene oxide) blocks are low, these block copolymers are amorphous, but, with increased molecular weight of the flexible blocks (2000 to 20 000), they become segregated in a separate phase and crystallise. The block copolymers exhibit a high strength (200–1000 kgf cm^{-2}) and a large relative elongation on rupture (800–100%).

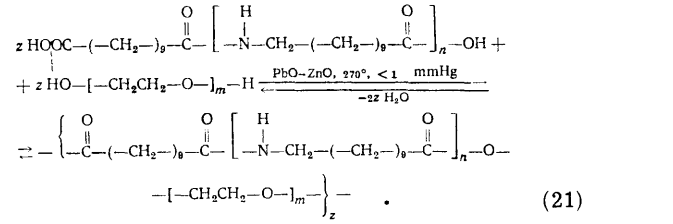
(d) Polycarbonate–poly(alkylene oxide) block copolymers. Regularly alternating block copolymers containing rigid oligocarbonate blocks based on 2,2-di-(4-hydroxyphenyl)propane and phosgene and flexible blocks of poly(ethylene oxide) or poly(tetramethylene oxide) are formed under the conditions of interfacial polycondensation from an oligocarbonate diol (2000 to 4700) obtained beforehand and an oligo(alkylene oxide) (1000–3000) with terminal chloroformate groups[88,89]. These block copolymers have fairly effective mechanical properties. Their strength is 100–150 kgf cm^{-2} and their relative elongation on rupture is >200%. The rate of crystallisation of oligocarbonate blocks in the copolymers is much higher than the rate of crystallisation of homopolycarbonate. There is a poly(alkylene oxide) amorphous phase in the block copolymers, but, when the molecular weight of the flexible blocks reaches 3000, a second crystalline phase is observed.

Irregular (ol + cm + cm-cl) polycarbonate–poly(alkylene oxide) block copolymers have been obtained by low-temperature polycondensation in solution from a mixture of oligo(alkylene oxide) diol [poly(ethylene oxide), poly(propylene oxide), and poly(tetramethylene oxide)], 2,2-di-(4-hydroxyphenyl)propane, and phosgene[90]. Block copolymers containing approximately 50 wt.% of oligo(ethylene oxide) blocks (4000–6000) have effective mechanical properties: an ultimate strength of 500 kgf cm^{-2} and a relative elongation on rupture of 600%. Block copolymers containing amorphous oligocarbonate blocks based on bisphenols with bulky bridge groups have been synthesised by the same method[91]. It is suggested[91] that the bulky norbornene rings in the rigid blocks constitute the nodes of a physical network which reduces the mobility of the macromolecules and imparts to the block copolymers the properties of thermoelastoplastic materials.

(e) Poly(arylene sulphone oxide)–poly(alkylene oxide) block copolymers. Regularly alternating poly(arylene sulphone oxide)–poly(ethylene oxide) block copolymers have been obtained[92] in accordance with Eqn.(21) from oligo(arylene sulphone oxide) diols (2400, 4600, and 9100) based on 2,2-di-(4-hydroxyphenyl)-propane and di-(4-chlorophenyl) sulphone and oligo(ethylene oxides) (400, 1000, 3000, and 15 000) with terminal acid chloride groups. Block copolymers with short flexible blocks (400–3000) consist of a single phase and have effective mechanical properties. For example, the copolymer containing 58 wt.% of rigid blocks with M.W. = 4600 and 42 wt.% of flexible blocks with M.W. = 3000 has an ultimate strength of 280 kgf cm^{-2} and a relative elongation on rupture of 460%. However, block copolymers with long (M.W. = 15 000) oligo(ethylene oxide) blocks have been found to contain a crystalline phase of the latter and such polymers have low values of the parameters characterising the mechanical properties; for example, the ultimate strength of a copolymer with rigid blocks having M.W. = 4600 and flexible blocks having M.W. = 15 000 is 180 kgf cm^{-2} and the relative elongation on rupture is 5%. Depending on composition, poly(arylene sulphone oxide)–poly(ethylene oxide) block copolymers swell in water by 1–120% and have effective antistatic properties.

Regularly alternating poly(arylene sulphone oxide)–poly(tetramethylene oxide) block copolymers obtained from oligo(arylene sulphone oxide) diols and oligo(tetramethylene oxides) with terminal chloroformate groups have been described[93].

(f) Polyamide–poly(alkylene oxide) block copolymers. Regularly alternating block copolymers with aliphatic polyamide blocks (usually polyamide 6 or polyamide 6,6) and poly(alkylene oxide) blocks are formed when oligo(alkylene oxides), in which the terminal hydroxy-groups have been substituted (in one or several stages) by isocyanate[94] or amino-groups[95], interact with oligoamines having terminal amino- or carboxy-groups. A dehydration reaction has been used recently to synthesise regularly alternating polyamide(11)–poly(ethylene oxide) block copolymers[96,97]:



(21)

The initial oligomers are incompatible, so that the reaction proceeds initially in a heterogeneous medium. The heterogeneity of the melt disappears if 10 wt.% of the finished block copolymer is added to the mixture of oligomers before the reaction[97]. The block copolymers can be used as thermoelastoplastic materials or as elastic fibres.

In order to reduce T_g and to improve the capacity of aromatic polyamides for being processed, multiblock irregular (ol + cm-fgs + cm-cl), irregular (ol + fgs + cm-fgs + cm-cl), and three-block polymetaphenyleneisophthalamide–poly(ethylene oxide) block copolymers have been synthesised[98]. They consist of two phases: the poly(ethylene oxide) phase (molecular weight of blocks 1000–6000) is dispersed in the continuous polyamide phase[99,100]. The rheological and physicomechanical properties of the copolymers have not been published as yet.

(g) Polystyrene–poly(alkylene oxide) block copolymers. Multiblock regularly alternating polystyrene–poly(ethylene oxide) block copolymers have been obtained by increasing the chain lengths of three-block poly(ethylene oxide)–polystyrene–poly(ethylene oxide) copolymers of the polymerisation type having terminal hydroxy-groups with phosgene or a dicarboxylic acid dichloride[101]. Another method of synthesis of the block copolymers consists in the interaction of an oligostyrene di-isocyanate (2000–6000) with an oligo(ethylene oxide)diol (400–6000).[102] The block copolymers exhibit

an enhanced capacity (compared with polystyrene) for absorbing atmospheric moisture, which increases with increasing content of hydrophilic blocks. Polystyrene–poly(ethylene oxide) copolymers are amorphous, but, during isothermal annealing, the segregation of oligo(ethylene oxide) blocks in a separate phase initiated by crystallisation is observed. The maximum rate of crystallisation has been noted for blocks with M.W. = 6000: they form twofold and threefold structures incorporated in crystalline domains [103]. The block copolymers containing flexible blocks with M.W. = 2000 do not crystallise. The short blocks in such copolymers act as plasticisers, lowering the temperature of the α-transitions of the polystyrene blocks [104].

Regularly alternating polystyrene–poly(ethylene oxide) block copolymers can also be obtained by converting a "living" oligostyrene with terminal carbanionic groups under the influence of an excess of phosgene into a bischloroformate with its subsequent polycondensation with an oligo(ethylene oxide) diol [105].

Two-block and three-block polystyrene–poly(tetramethylene oxide) block copolymers have been obtained by the reaction of a "living" oligo(tetramethylene oxide) cation or dication and a "living" oligostyrene anion [106]. Multiblock regularly alternating polystyrene–poly(tetramethylene oxide) block copolymers are formed in the interaction of an oligo(tetramethylene oxide) dication and an oligo-styrene dicarboxylate, used instead of the oligostyrene dianion, because the latter is involved in side reactions [107] [Eqn.(22)]. Block copolymers having an analogous structure have been obtained by the interaction of oligostyrene [108] or oligo-α-methylstyrene [109] dianions with an oligo(tetramethylene oxide) dication obtained with the aid of the $AgPF_6$–alkyl bromide initiator. It is suggested that the reaction between "living" polymeric dianions and dications is accompanied by the elimination of a tetrahydrofuran molecule.

(h) Cellulose–poly(alkylene oxide) block copolymers. Regularly alternating cellulose–poly(alkylene oxide) block copolymers have been obtained by the reaction of substituted, for example, acetylated, cellulose oligomers having terminal hydroxy-groups with oligo(alkylene oxides) having terminal isocyanate groups [110–112] [Eqn. (23)]. Acetylation of cellulose makes it possible to carry out its oligomerisation and at the same time increase its resistance to biodegradation. If the block copolymers synthesised are subjected to deacetylation, the result is the formation of cellulose–poly(propylene oxide) block copolymers capable of undergoing enzymatic hydrolysis. Biodegradation of the block copolymers takes place under these conditions many times faster than the degradation of cellulose [111,112].

The introduction of oligomeric cellulose blocks and other polymers capable of biodegradation (starch, casein, gelatin, etc.) into the macromolecules of the polymers used to prepare mass consumption articles is of considerable interest in view of the problem of the protection of the environment. It appears that the synthesis of block copolymers capable of biodegradation and having acceptable physicomechanical properties may become one of the approaches to the solution of this problem.

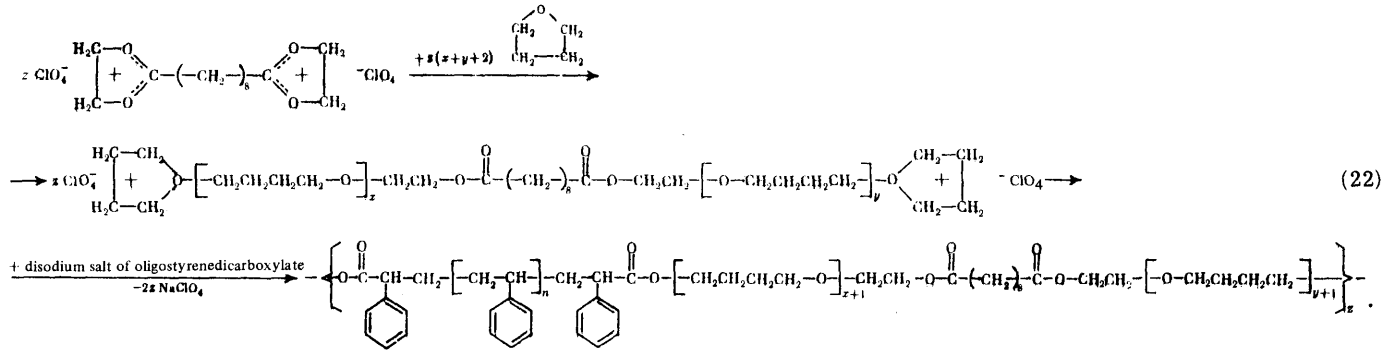
2. Block Copolymers Containing Aliphatic Polyester Blocks

Aliphatic polyesters are elastic crystallisable polymers with low melting and glass points. In this sense they are important for the synthesis of block copolymers of the polycondensation type, although their properties are inferior to those of polyethers.

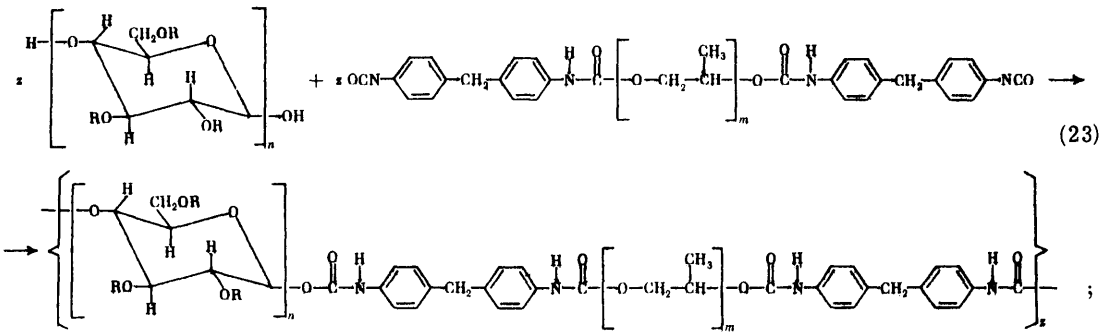
(a) Polyurethane–polyester block copolymers. These block copolymers consist of rigid polyurethane blocks, obtained from a di-isocyanate and a low-molecular weight glycol, and flexible polyester blocks with M.W. = 1000–3000. Oligo(ethylene adipate), oligo(ethylene sebacate), oligo(tetramethylene adipate), etc. are usually employed as the initial oligoesters with terminal hydroxy-groups. Among polyurethane–polyester block copolymers, irregular (ol + cm-fgs + cm-cl) copolymers [Eqn.(18)] have acquired the greatest practical importance. In contrast to the analogous polyurethane–polyether block copolymers, segmented polyurethanes based on aliphatic polyesters exhibit a much lower hydrolytic stability [54–56].

(b) Polyurea–polyester block copolymers. These block copolymers are synthesised in accordance with the same principle as polyurethane–polyester block copolymers. The difference is that, instead of a low-molecular-weight glycol [Eqn.(18)], a diamine is used [54–56].

(c) Polycarbonate–polyester block copolymers. Regularly alternating polycarbonate–poly(ethylene adipate) block copolymers have been obtained by the reaction of oligo(ethylene adipate) bischloroformate with oligocarbonatediol [88]. Irregular (ol + cm + cm-cl) block copolymers have been obtained by the reaction of a mixture of oligocarbonatediol based on 2,2-di-(4-hydroxyphenyl)propane and an oligocaprolactonediol with phosgene [113].



(22)



(23)

n = 20 - 30; R = —COCH$_3$, —CONHC$_6$H$_5$, —CH$_3$, or —CH$_2$C$_6$H$_5$

These block copolymers have the properties of thermoelastoplastic materials. Annealing of the specimens appreciably accelerates the crystallisation of the polycarbonate domains uniformly distributed in the amorphous polyester phase.

A series of other irregular polycarbonate–polycaprolactone block copolymers containing polycarbonate blocks based on 2,2,4,4-tetramethylcyclobutanediol [114] and various bisphenols [115] have also been described.

(d) Polyamide–polyester block copolymers. Regularly alternating polyamide(12)–poly(ethylene adipate) block copolymers have been obtained in the melt from aliphatic oligoamides with terminal carboxy-groups and oligo(ethylene adipates) with terminal hydroxy-groups [116]. The block copolymers exhibit a high strength and elasticity. The structure of the copolymers is appreciably influenced by exchange side processes.

Block copolymers consisting of rigid aromatic polyamide blocks and flexible polycaprolactone blocks have been obtained by the reaction of an oligocaprolactone having terminal isocyanate groups and an oligoamide having terminal amino-groups [117].

3. Block Copolymers Containing Diene Polymer Blocks

Polydienes (polybutadiene, polyisoprene, polypiperylene, polychloroprene, etc.) are elastic polymers capable of crystallisation only at very low temperatures. Owing to the high mobility of their macromolecules, polydienes have low glass points; for example $T_g = -108°C$ for *cis*-1,4-polybutadiene. The possibilities for the synthesis of block copolymers containing flexible polydiene blocks have greatly increased recently in connection with the development of the industrial manufacture of living "rubbers" [118].

(a) Polyurethane–polydiene and polyurea–polydiene block copolymers. Among segmented polyurethanes, block copolymers consisting of rigid oligourethane or oligourea blocks and flexible oligodiene blocks (polybutadiene, polyisoprene, copolymers of butadiene with acrylonitrile and isoprene, etc.) have been acquiring increasing importance recently. These block copolymers have the properties of thermoelastoplastic materials and exhibit a high hydrolytic stability [55,56,61].

(b) Polyamide–polydiene block copolymers. Irregular (ol-1 + ol-2 + cl) poly-ε-caprolactam–polybutadiene block copolymers have been synthesised [119]; oligo-ε-caprolactam with terminal amino-groups, oligobutadienediol, and 4,4′-diphenylmethane di-isocyanate were used as the initial compounds.

(c) Polyimide–polydiene block copolymers. Irregular (ol + cm + cm-cl) multiblock polyimide–polybutadiene block copolymers have been obtained from an oligobutadiene having terminal amino-groups, *m*-phenylenediamine, and the dianhydride of benzophenonetetracarboxylic acid [120].

4. Block Copolymers Containing Aliphatic Polysulphides

Aliphatic polysulphides (thiokols) are elastic polymers capable of crystallising on extension; the glass points of polysulphide rubbers are in the range from −20° to −60°C. Both polydisulphides and polytetrasulphides are special purpose rubbers characterised by high resistance to swelling in solvents, fuels, and oils, resistance to ozone and sunlight, and reduced permeability to moisture and gases.

(a) Polyurethane–polysulphide block copolymers. Block copolymers consisting of rigid oligourethane and flexible aliphatic oligosulphide blocks are obtained using oligosulphidedithiols, di-isocyanates, and glycols as the initial compounds. Polyurethane–polysulphide block copolymers have lower values of T_g compared with polyurethane–polyester block copolymers and exhibit a satisfactory radiation stability [121].

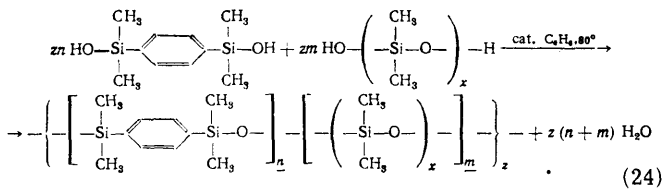
(b) Polyimidothioether–polysulphide block copolymers. Irregular (ol + cm-fgs + cm-cl) polyimidothioether–polysulphide block copolymers have been obtained from an oligosulphidedithiol, bismaleimide, and hydrogen sulphide [122]. These block copolymers exhibit the properties of thermoelastoplastic materials and are insoluble in organic solvents. A great obstacle to the processing of block copolymers via the melt is the low thermal stability of the polysulphide blocks, whose degradation begins at 200°C.

5. Block Copolymers Containing Polyorganosiloxane Blocks

(a) Polyurethane–polyorganosiloxane and polyurea–polyorganosiloxane block copolymers. Segmented polyurethanes containing flexible polyorganosiloxane blocks exhibit an enhanced thermal stability compared with polyurethanes based on oligoethers,

have effective low-temperature properties, and exhibit a high resistance to tearing[54].

(b) Polytetramethylsilphenylenesiloxane–polydimethylsiloxane block copolymers. Irregular (ol + m-cm) polytetramethyl-*para*-silphenylenesiloxane–polydimethylsiloxane block copolymers have been obtained in the presence of non-equilibrating catalysts from oligodimethylsiloxanediol and tetramethyl-*para*-silphenylenesiloxane[123]:



(24)

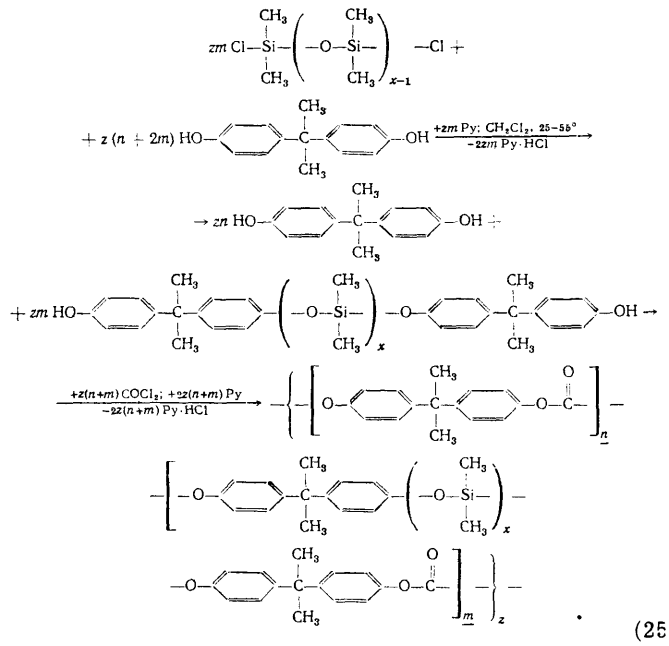
The block copolymers obtained comprise two phases: the continuous phase consists of amorphous polydimethylsiloxane blocks and the disperse phase is made up of crystalline domains of polytetramethyl-*para*-silphenylenesiloxane blocks which melt in the temperature range from 25° to 139°C, depending on the composition of the copolymers[124]. The block copolymers manifest the properties of thermoelastoplastic materials, have a strength of 70 to 200 kgf cm^{-2}, and a relative elongation on rupture of 500–960%.[125]

(c) Polystyrene–polydimethylsiloxane block copolymers. Regularly alternating polystyrene–polydimethylsiloxane block copolymers of the type $-(A-B-A-)_n$ have been obtained by the interaction of "living" polydimethylsiloxane–polystyrene–polydimethylsiloxane block copolymers of the polymerisation type with chain elongating agents such as diacetoxydiphenylsilane, dialkyldichlorosilanes, or dichloromethyltrifluoropropylsilane[126,127]. These block copolymers constitute a two-phase system comprising a continuous polydimethylsiloxane phase with $T_g = -120$°C and a disperse polystyrene phase with $T_g = 50$°C. The polymers have the properties of thermoelastoplastic materials, possess effective dielectric properties, and exhibit a high permeability to gases[128].

Regularly alternating block copolymers of the type $-(-A-B-)_n-$ have been obtained by the dehydropolycondensation of polydimethylsiloxane–polystyrene–polydimethylsiloxane A–B–A block copolymers having terminal hydroxy-groups in the presence of a catalyst[129].

(d) Poly-α-methylstyrene–polydimethylsiloxane block copolymers. Regularly alternating poly-α-methylstyrene–polydimethylsiloxane block copolymers of the type $-(-A-B-)_n-$ have been obtained by the polycondensation of oligo-α-methylstyrenediols and oligodimethylsiloxanes having terminal dimethylamino-groups in chlorinated aromatic solvents at 120° to 180°C.[130] The low reactivity of the hydroxy-groups in the aliphatic terminal units of oligo-α-methylstyrenediols may be increased with the aid of carbon dioxide, which catalyses the reaction. The block copolymers consist of two phases and have the properties of thermoelastoplastic materials. The replacement of polystyrene blocks by poly-α-methylstyrene blocks ($T_g = 170$°C) made it possible to extent the temperature range where the block copolymers are useful from between −100°C and +50°C to between −100°C and +130°C.

(e) Polycarbonate–polydimethylsiloxane block copolymers. Irregular (ol + cm-fgs + cm) polycarbonate–polydimethylsiloxane block copolymers have been obtained by treating with phosgene a mixture of 2,2-di-(4-hydroxyphenyl)propane and an oligodimethylsiloxane having terminal phenolic groups[131–133]:



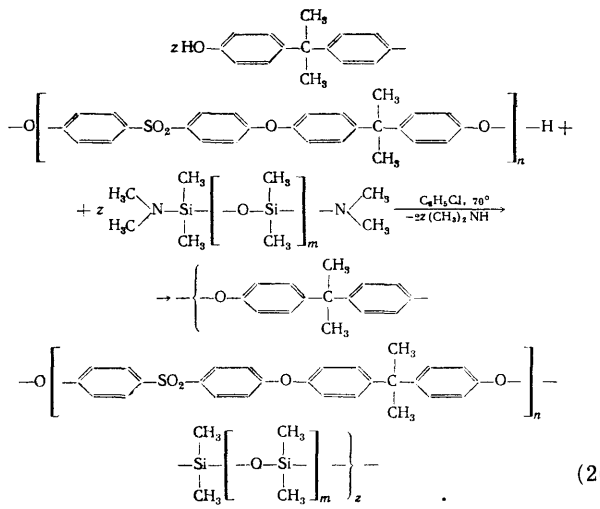
(25)

The block copolymers consist of two phases and manifest the properties of thermoelastoplastic materials. With increase in the content of rigid oligocarbonate blocks from 35 to 85%, the ultimate strength rises from 70 to 420 kgf cm^{-2} and the relative elongation on rupture falls from 800 to 100%.[133] The glass point of the continuous polydimethylsiloxane phase depends little on the length of the flexible blocks and is in the region of −110°C; on the other hand, T_g for the polycarbonate domains depends markedly on the length of the rigid blocks, varying from 60°C for blocks with five elementary units in the chain to 140°C for blocks with 46 repeating units. Crystallisation of the polycarbonate domains is observed when the block copolymer films are kept in ethyl methyl ketone or its vapour[134]. The solvent greatly influences the morphology of the block copolymer films obtained by casting from solutions[133]. The thermal stability of the block copolymers is somewhat inferior to that of homopolycarbonate[135]. Polycarbonate–polydimethylsiloxanes have useful dielectric properties[136] and a high permeability to gases[137]. Membranes based on them are used in apparatus designed for the enrichment of air in oxygen and for the oxygenation of blood. The block copolymers can be employed as coatings and adhesives[131].

Regularly alternating[138] and irregular (ol + cm-fgs + cm) polycarbonate–polydimethylsiloxane block copolymers based on cardobisphenols[139] and 2,2,4,4-tetramethylcyclobutane-1,3-diol[140] have also been obtained.

(f) Poly(arylene sulphone oxide)–polydimethylsiloxane block copolymers. Regularly alternating poly(arylene sulphone oxide)–polydimethylsiloxane block copolymers have been obtained by the interaction of equimolar amounts of an oligo(arylene

sulphone oxide)diol and an oligodimethylsiloxane having terminal dimethylamino-groups[141,142]:



(26)

Such block copolymers consist of two phases and exhibit the properties of thermoelastoplastic materials. The glass point of the polydimethylsiloxane phase is −120°C and that of the poly(arylene sulphone oxide) phase is +160°C, the ultimate strength of block copolymers containing 50–70 wt.% of the organosilicon phase is 100–180 kgf cm^{-2} and the relative elongation is 500–350%.[142] The block copolymers are resistant to hydrolysis, have a high thermal stability[142] and useful dielectric properties, and exhibit a high permeability to gases[143]. Poly(arylene sulphone oxide)–polydimethylsiloxane block copolymers can be used as film materials, as thermoelastoplastic substances with a wide range of working temperatures (from −120° to +160°C),[142] and as additives to poly(arylene sulphone oxides) (which increase their impact strength)[144].

(g) Poly(phenylene oxide)–polydimethylsiloxane block copolymers. Three-block poly(phenylene oxide)–polydimethylsiloxane block copolymers of the type A–B–A have been obtained by the reaction of an oligo(phenylene oxide) having a terminal hydroxy-group and an oligodimethylsiloxane having terminal isopropylamino-groups[145]. The block copolymers may be used as electrically insulating and thermally shrinkable films.

(h) Polyester–polydimethylsiloxane block copolymers. Regularly alternating poly(hexamethylene sebacate)–polydimethylsiloxane block copolymers have been obtained by the reaction of oligo(hexamethylene sebacate)diols and oligodimethylsiloxanes having terminal dimethylamino-[146] or chloro-groups[147]. The block copolymers consist of two phases. The rigid phase with T_m = 57°C is highly crystalline and consists of spherulites.

Regularly alternating block copolymers containing rigid blocks based on 2,2-di-(4-hydroxyphenyl)propane and isophthalic or terephthalic acid dichloride consist of two phases and exhibit the properties of thermoelastoplastic materials. The glass points of the flexible and rigid phases are −125°C and between +120°C and +135°C respectively and the melting point of the rigid phase is 295 and 260°C for the copolymers obtained from the dichlorides of terephthalic and isophthalic acids respectively[148].

Regularly alternating block copolymers containing amorphous blocks based on bisphenols and phthalic acid dichlorides have also been synthesised. Polyarylate–polydimethylsiloxane block copolymers are made up of two phases and exhibit the properties of thermoelastoplastic materials[149–151]. A high degree of segregation of the rigid and flexible blocks is observed in the block copolymers; the domains of the polyarylate phase have a diameter of approximately 160 Å. Polyarylate–polydimethylsiloxanes have high hydrolytic[152] and thermal[153] stabilities, effective electrically insulating properties, and a high permeability to gases. The properties of the resulting films are greatly influenced by the solvent[154].

(i) Polyamide–polydimethylsiloxane and polyimide–polydimethylsiloxane block copolymers. Regularly alternating polyamide–polydimethylsiloxane block copolymers have been obtained by the reaction of oligoamidediols based on α-amino-acids and oligodimethylsiloxanes having terminal dimethylamino-groups[155] and by the reaction of oligo-*meta*-phenyleneisophthalamides having terminal amino-groups and oligodimethylsiloxanes having terminal acid chloride groups[98]. The synthesis of regular (ol + fgs + cm-fgs + cm-cl) poly-*meta*-phenyleneisophthalamide–polydimethylsiloxane block copolymers has been described[98].

Regularly alternating polyimide–polydimethylsiloxane block copolymers have been synthesised by the reaction of oligoimides having terminal anhydride groups and oligodimethylsiloxanes having terminal aminoalkyl groups[156].

B. THERMOPLASTIC BLOCK COPOLYMERS

Thermoplastic block copolymers consist of thermoplastic polymer blocks.

1. Block Copolymers Containing Polycarbonate Blocks

(a) Polycarbonate–polyurethane block copolymers. Irregular (ol + cm + cm-cl) polycarbonate–polyurethane block copolymers have been obtained by the reaction with phosgene of a mixture of an aromatic oligourethanediol and 2,2-di-(4,4-hydroxyphenyl)propane or by the reaction of a mixture of an aromatic oligourethane bischloroformate and phosgene with 2,2-di-(4-hydroxyphenyl)propane[157].

Articles made from modified polycarbonates (for example, the base used for photographic film and recording tape) exhibit a high stability as regards size but, owing to the presence of aromatic polyurethane blocks, their thermal stability is reduced.

(b) Polycarbonate–polystyrene block copolymers. Regularly alternating polycarbonate–polystyrene block copolymers have been obtained by the interaction of oligostyrene bischloroformates with oligocarbonatediols[88].

Irregular (ol + cm + cm-cl) block copolymers have been synthesised by the reaction of a mixture of an oligostyrenediol [obtained by treating a "living" oligostyrene with phosgene and then with an excess of 2,2-di-(4-hydroxyphenyl)propane] and 2,2-di-(4-hydroxyphenyl)propane with phosgene[158]. Oligostyrenediols having molecular weights of 2900, 4100, and 9300 have been used to synthesise block copolymers. It was found that at 250°C the melts of the block copolymers have lower viscosities than that of the homopolycarbonate. The decrease of the viscosity

of the melt depends to a greater extent on the content of oligostyrene blocks (19, 22, and 29 wt.%) in the block copolymer than on their molecular weight.

(c) Polycarbonate–poly(phenylene oxide) block copolymers. Three-block polycarbonate–poly-(2,6-dimethylphenylene oxide) block copolymers of the type A–B–A having effective physicomechanical properties have been obtained by the reaction of an oligo-(phenylene oxide) having a terminal hydroxy-group with an oligocarbonate bischloroformate [159].

(d) Polycarbonate–polyester block copolymers. Irregular (ol + cm + cm-cl) polycarbonate–poly(ethylene terephthalate) block copolymers with satisfactory physicomechanical properties have been obtained in the melt from a mixture of oligo(ethylene terephthalate)diol, 2,2-di-(4-hydroxy-phenyl)propane, and diphenyl carbonate [160].

2. Block Copolymers Containing Poly(arylene sulphone oxide) Blocks

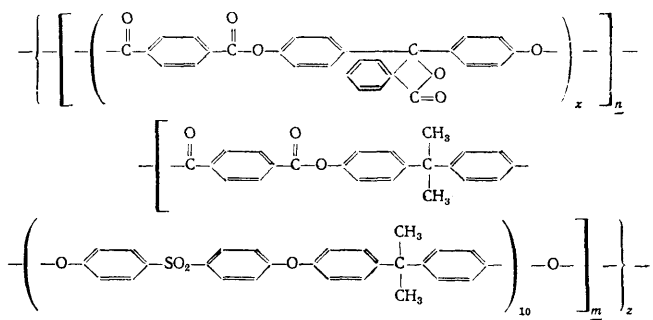
(a) Poly(arylene sulphone oxide)–polycarbonate block copolymers. Irregular (ol + cm + cm-cl), irregular (ol-1 + ol-2 + cl), and regularly alternating poly(arylene sulphone oxide)–polycarbonate block copolymers have been synthesised in three different ways [161]. The initial compounds were oligo(arylene sulphone oxide)diols based on 2,2-di-(4-hydroxyphenyl)-propane and di-(4-chlorophenyl) sulphone with molecular weights from 5000 to 26 000, oligocarbonatediols or oligo-carbonate bischloroformates based on 2,2-di-(4-hydroxy-phenyl)propane and phosgene with molecular weights from 5000 to 22 000, di-(4-hydroxyphenyl)propane, and phos-gene. The resulting block copolymers of all three types and any composition were single-phase, despite the fact that the mixtures of the corresponding homopolymers and also the mixtures of the oligomers were heterophase. It has been suggested [162] that the formation of a second phase in the system can begin when oligomers with molecular weights greater than 22 000–26 000 are used. The glass points of the single-phase block copolymers depend on their composition and vary from 175° to 184 °C. Further-more, T_g depends also on the method of synthesis of the block copolymer; in particular, among irregular (ol + cm + cm-cl) and irregular (ol-1 + ol-2 + cl) block copoly-mers of the same composition, the irregular (ol-1 + ol-2 + cl) copolymer has a higher T_g. [161] Exposure of the specimens to acetone leads to the selective crystallisation of the oligocarbonate blocks, whereupon a single value of T_g and a single melting point T_m of the crystallites (T_m = 235 °C) are observed.

(b) Poly(arylene sulphone oxide)–polystyrene block copolymers. Irregular (ol-1 + ol-2 + cl) poly(arylene sulphone oxide)–polystyrene block copolymers have been synthesised by the reaction of a mixture of oligo(arylene sulphone oxide)diol based on 2,2-di-(4-hydroxyphenyl)propane and di-(4-chlorophenyl)-sulphone and an oligostyrenediol with phosgene (Noshay and McGrath [8], p. 312). The block copolymers synthe-sised from oligomers with a molecular weight less than 4000 are single-phase, but if the molecular weight of the oligomer is greater than 4000, the block copolymers con-sist of two phases.

(c) Poly(arylene sulphone oxide)–poly-(phenylene oxide) block copolymers. Three-block poly(arylene sulphone oxide)–poly(phenylene oxide) block copolymers of the type A–B–A, suitable for the manufacture of cast articles and films, have been synthe-sised from oligo(phenylene oxides) having a terminal hydroxy-group and oligo(arylene sulphone oxides) having terminal acid chloride, chloroformate, or isocyanate groups [163].

(d) Poly(arylene sulphone oxide)–poly-ester block copolymers. Irregular (ol + cm + cm-cl) poly(arylene sulphone oxide)–poly(butylene tere-phthalate) block copolymers have been obtained by the reaction in boiling trichlorobenzene of an oligo(arylene sulphone oxide), having terminal acid chloride groups, and terephthalic acid dichloride with butylene glycol (Noshay and McGrath [8], p. 324). The glass point of the mixed amorphous phase in the block copolymers is 139 °C and the melting point of the crystalline polyester phase is 200 °C.

Poly(arylene sulphone oxides)–polyarylate block copolymers have been obtained in three different ways: (a) from pre-synthesised heterofunctional oligo(arylene sulphone oxides) and oligoarylates; (b) from homofunc-tional oligomers and the corresponding chain lengthening agents; (c) by introducing oligo(arylene sulphone oxides) into a mixture of initial low-molecular-weight compounds [164]:



where x is 10 for regularly alternating block copolymers, a multiple of 10 for irregular (ol-1 + ol-2 + cl) block copolymers, and ≥1 for irregular (ol + cm + cm-cl) block copolymers. Poly(arylene sulphone oxide)–polyarylate block copolymers consist of a single phase, while mix-tures of the corresponding homopolymers and oligomers are heterophase. For low contents of oligo(arylene sulphone oxide) blocks in irregular (ol + cm + cm-cl) block copolymers, Young's modulus of elasticity, the ultimate tensile strength, and the relative elongation increase. This effect is very similar to the "antiplasticisation" effect observed for rigid-chain polymers plasticised by low-molecular-weight plasticisers.

It is especially interesting that the viscosity of melts of poly(arylene sulphone oxide)–polyarylate block copolymers varies non-additively with respect to the change in com-position. A characteristic feature is a minimum in the viscosity of the melt for a relatively low content of oligo-(arylene sulphone oxide) blocks in the copolymers. The rheological characteristics of block copolymers of this composition are close to those of poly(arylene sulphone oxide) [165].

3. Block Copolymers Containing Polystyrene Blocks

Polystyrene–polycarbonate and polystyrene–poly(arylene sulphone oxide) block copolymers were described above.

(a) Polystyrene–polyester block copolymers. Irregular (ol + cm + cm-cl) polystyrene–poly(ethylene terephthalate) block copolymers have been obtained at 280°C in the presence of a catalyst from a mixture of an oligostyrenediol, ethylene glycol, and dimethyl terephthalate. The block copolymers consist of two phases; with increased content of crystallising polyester blocks in the copolymers, a uniform increase of the melting point and density of the block copolymers is observed[166].

(b) Polystyrene–polyamide block copolymers. Irregular (ol + m-cl) polystyrene–polyamide 6 and polystyrene–polyamide 6,6 block copolymers have been obtained by the interaction in the melt of a diammonium adipate salt derivative of oligostyrene (obtained by the interaction of oligostyrenediamine with adipic acid) with ϵ-aminocaproic acid or hexamethylene adipate (HA salt) respectively[166]. The block copolymers consist of an amorphous polystyrene phase and a crystalline polyamide phase. With increase of the content of crystallising blocks in the copolymers, a uniform increase of the melting point and density of the block copolymers is observed.

4. Block Copolymers Containing Polyether Blocks

Poly(phenylene oxide)–polycarbonate and poly(phenylene oxide)–poly(arylene sulphone oxide) block copolymers were described above.

Apart from these block copolymers, copolymers consisting of blocks of sulphonated polyethers, for example, those based on 2,2-di-(4-hydroxyphenyl)propane and 1,4-dichlorobutane, and polyester blocks, for example blocks based on ethylene glycol and dimethyl terephthalate, are known[167]. Irregular (ol + cm + cm-cl) polyether–polyester block copolymers have been obtained by the interaction of a mixture of a sulphonated polyetherdiol and glycol with dimethyl terephthalate. These block copolymers may be used as additives which increase the affinity of polyether [polyester?] fibres for basic dyes.

5. Block Copolymers Containing Polyester Blocks

Polyester–polycarbonate, polyester–poly(arylene sulphone oxide), polyester–polystyrene, and polyester–polyether block copolymers were described above.

Regularly alternating copolymers consisting of poly(ethylene terephthalate) and polyamide 6 [168] or polyamide 6,10 [169] blocks are also known. The block copolymers are obtained by the interaction of oligoamidedicarboxylic acids with oligoesterdiols[168] or by the reaction of oligoamidediamines with oligoesterdiacylchlorides[169].

C. ELASTOMERIC BLOCK COPOLYMERS

Elastomeric block copolymers consist of flexible rubberlike polymer blocks. A limited number of such block copolymers are known at the present time.

1. Polydimethylsiloxane–Poly(alkylene oxide) Block Copolymers

Linear polydimethylsiloxane–poly(alkylene oxide) block copolymers are formed when oligo(alkylene oxide)-diols interact with oligodimethylsiloxanes having acetoxy-,[170] dialkylamino-,[171] or isocyanate [172] end groups. These block copolymers are widely used as stabilisers ("silicone" surfactants) of polyurethane foams and also for the treatment of textile fibres (Allport and Janes[7], p. 342).

2. Polydimethylsiloxane–Polyester Block Copolymers

Irregular (ol + cm + cm-cl) polydimethylsiloxane–poly(butylene sebacate) block copolymers have been obtained from an oligodimethylsiloxane having terminal chloro-groups, butylene glycol, and sebacic acid dichloride; they may be used as loosening and levelling agents in electrophotographic compositions[173].

V. THREE- AND MULTI-TYPE BLOCK COPOLYMERS

Three-type block copolymers consist of polymer blocks of three different types [polyethers (polyesters?), polyorganosiloxanes, polydienes, polycarbonates, polyamides, etc.].

Very limited information is available at present about block copolymers of this kind; for example, the synthesis of five-block three-type polystyrene (A)–polybutadiene (B)–polyurea (C) block copolymers of the type A–B–C–B–A has been described[174], but no syntheses of multitype block copolymers have been published. In the future the synthesis of three- and multi-type block copolymers of the polycondensation type will undoubtedly be important in the manufacture of polymeric materials with a specified set of properties.

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