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Macromolecular and Oligomeric Compounds as Stabilisers for Polymers

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The preparation is described of various types of macromolecular and oligomeric compounds, together with their use as stabilisers for polymers (to heat and light as well as to oxidation). Possible mechanisms of their action are discussed. Carbon-chain polymers, macromolecular and oligomeric compounds containing elements in Groups IV–VI of the Periodic System (silicon, tin, nitrogen, phosphorus, oxygen, and sulphur), and polymers having a system of conjugated double bonds are considered as stabilisers. These products have the advantages over the usual stabilisers of being polyfunctional, non-volatile, long lived in the polymers, and in individual cases considerably more effective. A list of 221 references is included.

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I. INTRODUCTION

Polymeric materials, though possessing valuable physical and mechanical properties, have the important defect of undergoing various types of aging under the influence of heat, light, atmospheric oxygen, etc. One method for improving the operational durability of these materials is to introduce stabilisers into them. Various oligomeric and polymeric compounds have been proposed comparatively recently for this purpose, in addition to the usual stabilisers. As early as 1964 Kargin suggested that macromolecular additives to polymers were most effective for regulating almost any processes in them [1]. The chief advantages of macromolecular and oligomeric stabilisers can be summarised as follows.

1. By interacting with the polymer during its degradation such stabilisers may prevent a decrease in the molecular weight of the material [1] associated both with depolymerisation and with the chance rupture of macromolecular chains.

2. Macromolecular and oligomeric stabilisers possess valuable technical properties—non-volatility, prolonged retention in the polymer, and, when of similar chemical structure, good compatibility with the latter.

3. In several cases these stabilisers are more effective than analogous compounds of low molecular weight.

The chief obstacle to the widespread application of polymeric and oligomeric stabilisers is probably the difficulty of blending them with the stabilised polymer, and also the possible adverse influence of degradation products of these stabilisers.

Polymeric and oligomeric derivatives of elements in Groups IV–VI of the Periodic System—carbon, silicon, tin(IV), nitrogen, phosphorus(V), and oxygen, sulphur, selenium, tellurium(VI)—have now been suggested as stabilisers for plastics. A large number of novel heteroatomic polymers have been synthesised during recent years [2–4], many of which have still been little studied and have not found practical application. It must be expected that in the near future macromolecular derivatives of such elements as boron, germanium, lead, and antimony will considerably supplement the list of practically useful polymers in general and effective polymeric stabilisers in particular.

Mainly factual data on polymeric and oligomeric stabilisers have been published; very few investigations have been made on the mechanism of their action. The aim of the present Reviewers has been not only to assemble and systematise the available information but also to direct the attention of research workers to this new and interesting branch of the chemistry and technology of high polymers.

II. HETEROATOMIC MACROMOLECULAR AND OLIGOMERIC COMPOUNDS

1. Polyorganosiloxanes

Polyorganosiloxanes have been suggested comparatively recently for protecting polymeric materials from thermal and thermo-oxidative degradation and from the action of ultraviolet radiation. They possess great resistance to oxidation and high temperatures. Their own thermal stability is strongly influenced by the nature and number of the organic radicals attached to the silicon atom: methyl and ethyl groups lower the thermal stability of polyorganosiloxanes, whereas phenyl groups enhance it [5,6]. Chemical modification of polyalkenes by liquid polyorganosiloxanes [7–9] leads to an improvement in their stability towards aging by heat and light. Modification was effected by heat-treating either the crude polyalkene or manufactured articles in the liquid polyorganosiloxane. The first stage in the modification of (low-density) polyethylene is regarded as the production of free radicals by the oxidation of carbon–hydrogen bonds at tertiary carbon atoms. The resulting hydroperoxy-groups in turn oxidise the organic portion of the (stabiliser) molecules with the rupture of silicon–carbon bonds. Subsequent reactions yield Si–O–C groups, as is confirmed by the infrared spectra of the modified polyethylene (absorption in the region of 1077, 1044, and 936 cm^{-1}). Furthermore, polysiloxane units are grafted on also at double bonds, as evidenced by the diminished number of unsaturated groups in the modified polyethylene (disappearance of absorption in the region of 886 cm^{-1}). Thus the great stability of modified polyalkenes to all forms of aging is explained

by a decrease in the number of mobile hydrogen atoms at tertiary carbon atoms and by the formation of energetically stable siloxane bonds in the macrochains. Similar mechanisms are probably responsible for the action of liquid polyorganosiloxanes containing the units

$$[(CH_3)(OSnR_3)SiO]_n \qquad (I)$$

(where R is a C_1–C_{12} alkyl), [10,11] and also for those of polyphenyl(hydroxyphenylpropylphenoxy)silcane and polyphenylaluminosiloxane [12]. These compounds exert a strong stabilising effect at high temperatures and surpass industrial organotin stabilisers in effectiveness.

Poly(vinylidene chloride) preserves its colour well at 130°C in the presence of

$$R[-O-Si(CH_3)(C_6H_5)]_nOR \qquad (II)$$

where R = t-butyl or pentyl and $n = 1$–5. [13] Improving the stability of the liquid polyorganosiloxanes themselves to thermal oxidation may enhance their stabilising effect. Thus additions of 8-hydroxyquinoline–titanopolydimethylsiloxane increase the thermal stability of liquid polyorganosiloxanes by factors of 15–18. [14]

2. Tin-containing Polymers and Oligomers

Organotin compounds have become widely used for stabilising plastics based on poly(vinyl chloride). They improve the stability towards heat and light, and are antioxidants. An advantage of organotin stabilisers is that their decomposition products strengthen the stabilising effect; whereas the decomposition products of stabilisers not containing tin often accelerate the degradation of poly(vinyl chloride). [1,15] In fact, because of the presence of organic residues attached to the tin atom through an oxygen atom, a sulphur atom, or a carboxy-group, the double decomposition of organotin compounds with hydrogen chloride yields, depending on the nature of these residues, thiols, dienophilic reagents, epoxy-compounds, phenols, ethers, esters, and other products which themselves have a stabilising action. Effective organotin stabilisers of poly(vinyl chloride) combine the functions of an inhibitor of dehydrochlorination of the polymer, an acceptor of hydrogen chloride, and a dienophile [16,17]. Organotin stabilisers probably coordinate with segments of conjugated double bonds in the polymers, thereby ensuring that the polymer retains its original colour for a long time [18]. However, no convincing evidence has yet been found for this.

Increasing interest has recently been taken in polymeric organotin stabilisers, since they are usually more effective than the corresponding stabilisers of low molecular weight. They have the considerable advantages of almost complete non-toxicity and of insolubility in water. The mechanism of the stabilising action of polymeric organotin compounds has not been studied. It can only be assumed that their action is closely analogous to that of the corresponding simple compounds [1].

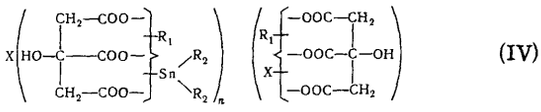
Poly(vinyl chloride) and copolymers of vinyl chloride are stabilised by polymeric alkyl(cycloalkyl)aryl-stannonic and -thiostannonic acids or their condensation products [19–22].

Polymeric organotin carboxylates and alkyl sulphides [23–26] are more effective than those of low molecular weight. Poly(vinyl chloride) resins are stabilised by the introduction of 0.1 -- 5.0 wt. % of the reaction product of a poly(alkyl(ene)tin oxide or dihalide) with an alkali-metal salt of lauric, thiobenzoic, β-mercaptopropionic, or octylthioglycollic acid or dodecanethiol [27,28]. Organotin compounds of formula [29]

$$R_1R_2R_3Sn[XSnR_4R_5]_mR_6 \qquad (III)$$

(where R_1–R_6 are hydrocarbon radicals (C_{1-30}) or OH groups, X = O or S, and $m = 0$–15) have also been used mixed with other stabilisers.

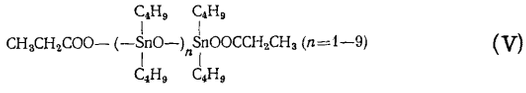
A polymeric organotin stabiliser, which improves the heat resistance of poly(vinyl chloride) and poly(vinylidene chloride), has been obtained by heating dibutyltin oxide with a polyester based on bicyclo[2,2,1]heptene-2,3-dicarboxylic acid (or its anhydride) and a glycol (ethylene, propylene, butylene, etc.). [30,31] The compounds



(IV)

(where X = H or an alkali metal, R_1 = Alk (C_{1-10}) or alkylene (C_{3-10}), R_2 = Alk (C_{1-20}), and $n = 1$–20), obtained from alkali-metal salts of citric monoesters and dialkyltin oxides or hydroxides, have been proposed as stabilisers against heat and light [32]. Poly(vinyl chloride) films stabilised with these compounds remain colourless after exposure to ultraviolet radiation for 500 h, whereas control films darkened after exposure for 20 h.

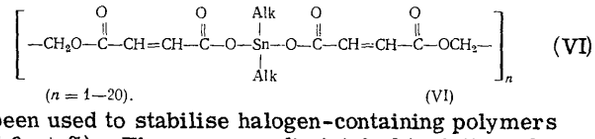
Polymeric dibutyltin dipropionate



(V)

was considerably more effective than its simple analogue ($n = 0$). [33–35]

Polymeric dialkyltin dicarboxylates



(VI)

have been used to stabilise halogen-containing polymers (0.5–5.0 wt. %). They possess diminished toxicity and blend well with the stabilised polymers [36,37]. Sulphur-containing organotin oligomers, e.g. polymeric tin dibutyl dithiodimaleate, have also been proposed as stabilisers [38,39].

3. Macromolecular and Oligomeric Compounds Containing Nitrogen

Among compounds containing nitrogen, aromatic amines have been most widely used as practical antioxidants. There is no generally accepted view on the mechanism of their action: formation of a charge-transfer complex between the aromatic ring of the inhibitor and the peroxy-radical responsible for the development of oxidative processes has been postulated [40]. Inactive products are formed when such a complex decomposes. A more soundly based hypothesis is that inhibition is accompanied by abstraction of hydrogen atoms from the amino-group [1,40,41]. This forms radicals stabilised by conjugation with the aromatic ring; their existence has been proved by means of electron spin resonance. The subsequent fate of these radicals depends both on their structure and on the reaction conditions. Several years' practical application of amines as antioxidants has shown that diamines in which the functional groups are close together are the most effective. The probable explanation [40] is that diamines are able to deactivate both active radicals

formed by the breakdown of a hydroperoxide, which prevents the development of degenerate branching processes. When a monofunctional inhibitor is used, only one of the radicals is deactivated, while the second escapes from the "cage" and continues the oxidation chain.

Products of the reaction of an epoxidised butadiene with *p*-aminodiphenylamine, 2-naphthylamine, aniline, *p*-aminophenol, and *p*-anisidine have been used to stabilise various classes of rubbers[42]. Considerably smaller quantities of the amine component are required when these compounds are employed than with the usual antioxidants. This is probably due to better compatibility of polymeric stabilisers with rubber. Low-temperature interfacial polycondensation of the bischloromethyl ether of ethylene glycol with hexamethylenediamine yields polyamine-ethers, whose use has been proposed[43,44] for stabilising synthetic rubber.

Polyalkenes have been stabilised by introducing polycarbodi-imides of molecular weight exceeding 500.[45,46]

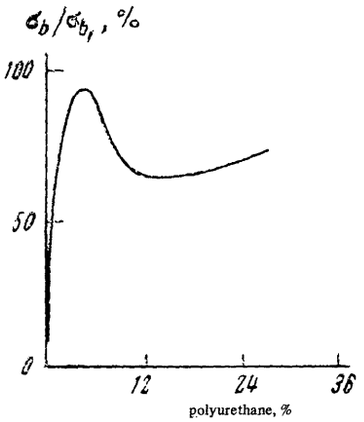


Figure 1. Dependence of tensile strength of acetylcellulose on content of added polyurethane[55], where σ_b is the tensile strength of the initial specimens and σ_{b_1} the tensile strength after exposure to ultraviolet radiation for 20 h.

Condensates of formaldehyde with respectively melamine, dicyanodiamide, urea, and thiourea have been suggested as stabilisers for polyacetals[47]. The molar ratio of the components in the condensation may vary within wide limits. The first two resins with a slight molar excess of formaldehyde (1.5–3.5 : 1) are acceptors of the formaldehyde liberated when the polymers are processed, and are thermally more stable. It is particularly noteworthy that polyacetals stabilised by the condensates do not discolour during processing. It is advisable to use these condensates mixed with known antioxidants and photostabilisers[47–50]. The thermal stability of polyformaldehyde is enhanced by the addition of polyacetalamides (M = 1000–10 000).[51]

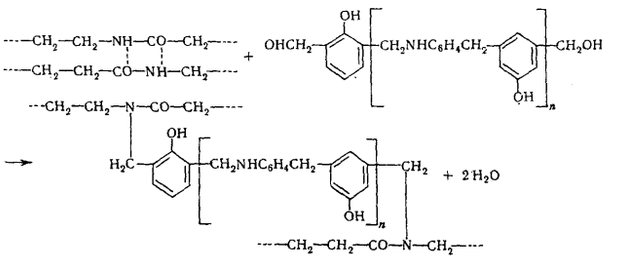
The use of copolymers of acrylamide (5–80 mole %) with styrene, alkyl acrylates, vinyl ketone, vinylnaphthalene, etc. has been proposed[52,53] for the thermal stabilisation of polyoxymethylene. The stabilised polyoxymethylene remained homogeneous and transparent.

The heat-resistance of polyurethane foams can be increased considerably by means of cyclic polyisocyanates obtained from aniline and formaldehyde or their derivatives[54].

The presence of polyurethanes—products of the condensation of tolylene di-isocyanate with ethylene glycol and of naphthylene di-isocyanate with triethylene glycol—diminishes appreciably the evolution of gas when acetylcellulose is exposed to ultraviolet radiation[55,56]. The variation in the tensile strength of exposed specimens indicates that the stabilising effect is considerably greater than could have been expected solely from the light-filtering action of the polyurethanes (Fig. 1). These products were more effective stabilisers for acetylcellulose than the phenyl salicylate usually employed industrially.

On ultraviolet exposure the polyurethane molecules are easily excited to a biradical triplet state (presence of phosphorescence in the luminescence spectra), and therefore become traps for free radicals formed by photolysis of the acetylcellulose. At low polyurethane contents this mechanism of stabilisation is decisive. In addition, the photodegradation of polyurethanes yields products having a system of conjugated bonds which exert a light-filtering effect. This latter mechanism of the stabilisation of acetylcellulose becomes dominant at high polyurethane contents. During exposure to ultraviolet the efficiency of polyurethanes as stabilisers does not diminish but, on the contrary, increases as degradation products accumulate. In principle any polyurethanes based on di- and polyisocyanates and polyhydroxy-compounds (glycols, polyethers) have a stabilising action. However, the energy of excitation of polyurethane molecules to the triplet state and the compatibility of a polyurethane with the polymer to be stabilised depend on the chemical structure of the polyurethane.

An aniline–phenol–formaldehyde resin has been suggested[57,58] for stabilising polyamide films. The stabilising effect is obviously due to the ability of the resin to react chemically with polyamides[59,60]:



which probably explains its efficiency as a photostabiliser. One cause of the aging of a polyamide film is the increase in the crystallinity of the polyamide with keeping. It may be supposed that the number of hydrogen bonds and the degree of crystallinity of the polyamide decrease in the presence of the ternary resin (1–2 wt.%).[61] Furthermore, the presence of phenolic and amine groups favours the appearance of inhibiting properties in the aniline–phenol–formaldehyde resin under certain conditions. This ternary resin, unlike other stabilisers (especially aromatic amines), does not increase the light absorption of polyamide films.

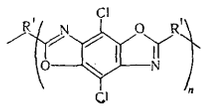
Polymeric antioxidants, whose efficiency has been tested in unfilled mixtures based on natural rubber, have been obtained by the reaction of a butadiene–methacrylaldehyde copolymer containing active aldehyde groups with

aniline and di-t-butylphenol[40]. A kinetic study of vulcanisation of the mixtures revealed that these products increase the degree of structuring of the mixtures. The explanation is that, in reacting with the peroxy-macroradicals of the rubber and forming complicated intermediate compounds, the polymeric antioxidants cross-link the molecular network of the vulcanised rubber, as it were, thereby stabilising it during oxidative degradation. Investigation of thermal aging showed polymeric antioxidants to be more effective than the usual stabilisers. They were found also to lengthen the induction period in the oxidation of pure and vulcanised rubber, as a consequence of their action on hydroperoxides. The similar chemical structure of polymeric antioxidants makes them readily compatible with vulcanised rubbers, with the absence of surface "blooming".

A few other examples of the use of oligomeric nitrogen-containing compounds as stabilisers should be mentioned. The elasticity and the heat-resistance of poly(vinyl chloride), poly(vinyl acetate), and their copolymers are improved by introducing a polyglutamate (M = 500–10 000)

$$[-NH-CH_2-(CH_2CH_2COOCH_2R)\,CO-] \qquad \text{(VII)}$$

where R = C_6H_5 or Alk (C_{5-21}).[62] Polymeric and simpler benzobisoxazole derivatives of the type



(VIII)

where R′ represents an alkylene or a phenylene radical, have been prepared[63,64]; they can be used as heat-stabilisers for halogenated polyalkenes.

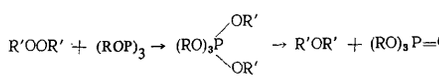
4. Phosphorus-containing Polymers and Oligomers

Organophosphorus compounds have recently been proposed as thermal stabilisers and antioxidants. Phosphorous esters have become widely used. The stabilising effect of tervalent phosphorus compounds is due to their great reactivity. These stabilisers can take part in various processes underlying the stabilisation of polymers —in inhibiting oxidative processes, suppressing the degenerate branching of an oxidation chain, breaking down chromophoric groups, and also suppressing the harmful action of derivatives of metals of variable valency, which are often present as impurities in polymers[65-68].

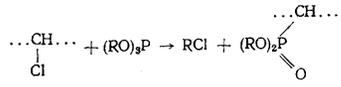
The stabilising action of phosphites in poly(vinyl chloride) at high temperatures (80–200°C) consists mainly in combining with the hydrogen chloride catalysing breakdown of the polymer

$$(RO)_3P + HCl \rightarrow (RO)_2POH + RCl,$$

and in reacting with polymeric peroxides to prevent degradation of the main chain of the polymer



Furthermore, chemically combined phosphorus is detected in the polymer on the thermal decomposition of poly(vinyl chloride). This is explained by the reaction



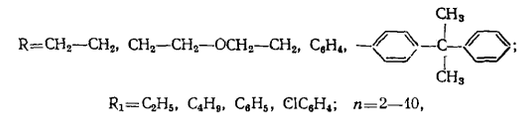
(the Arbuzov rearrangement), which may be catalysed by the alkyl chloride formed from the phosphite and hydrogen chloride. The rearrangement results in the replacement of labile chlorine atoms in the α-position to a double bond by groups more firmly bound to the polymer[69-73]. The efficiency of stabilisation increases with increase in the chain length of R.

Polymeric phosphites possess still more efficient inhibiting properties[74-78]. Polyphosphites of formula



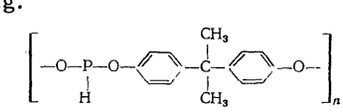
(IX)

where



blend well with many polymers (polyalkenes, poly(ethylene terephthalate), rubbers) and are firmly retained in them[79]. This confers on polyphosphites valuable properties not possessed by the usual antioxidants (alkyl aryl phosphites). Polyphosphites have been obtained by transesterification of such esters with dihydroxy-compounds[76,79], but the products hydrolyse in air, which makes their use difficult in practice. Polyphosphites obtained by transesterifying complete and mixed esters of phosphorous acid with alkylated bishydroxyphenyl sulphides are free from this defect. The inhibiting action of sulphur-containing polyphosphites has been assessed from the change in the rate constants for the chemical relaxation of tension, which is an unambiguous measure of the resistance of vulcanised butadiene–styrene rubbers to thermo-oxidative degradation. The polyphosphite obtained by transesterifying triphenyl phosphite with bis-4-hydroxy-2-methyl-5-t-butylphenyl sulphide, in which the oxygen-phosphorus bonds are shielded by t-butyl groups and are stable to hydrolysis, was especially effective[80].

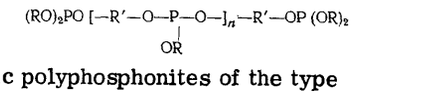
Not only complete polyphosphites but also intermediate structures, e.g.



(X)

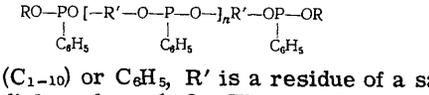
have been proposed for the stabilisation of poly(ethylene terephthalate). Addition of 1 wt.% to about one-quarter reduces the thermo-oxidative degradation of the polymer at ~ 260°C. The effectiveness of this stabiliser is probably due to the presence of oxidisable P–H bonds[81].

The colour of solutions of a copolymer of vinyl chloride with acrylonitrile is preserved in the presence of mixtures of alkylene oxides with polymeric organic phosphites of general formula



(XI)

or with organic polyphosphonites of the type

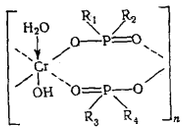


(XII)

where R = Alk (C_{1-10}) or C_6H_5, R′ is a residue of a saturated aliphatic diol, and n = 1–8. The use of lower alkylene oxides combined with polymeric organic phosphites and phosphonites improves the stability of resin solutions[82,83].

Halogenated resins have been stabilised by salts (cadmium, barium, lead, calcium, magnesium, zinc,

aluminium, tin, etc.) of organic or inorganic polyphosphoric acids[84]. Polymeric chromium phosphinate



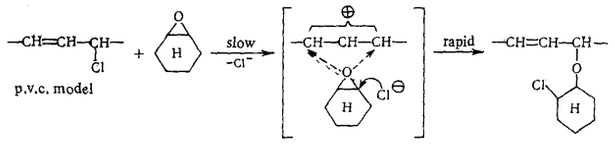
(R_1–R_4 = Ph, Me; $n > 1$) (XIII)

provides good protection for vinyl chloride polymers from ultraviolet radiation[85].

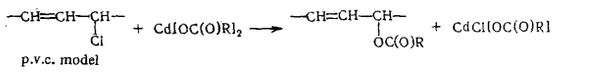
5. Polymers and Oligomers containing Epoxy-groups

The main types of epoxide stabilisers are glycidyl ethers—condensates of epichlorohydrin with phenols and aliphatic alcohols—and epoxidised esters of higher fatty acids.

The stabilising effect of epoxy-compounds and of their mixtures with the salts of aliphatic acids with Group II elements has been studied on model compounds—mixtures of 4-chlorohex-2-ene and 2-chlorohex-3-ene—that simulate a degraded poly(vinyl chloride) unit[86]. At 150°C the model compounds decomposed with the evolution of hydrogen chloride. Degradation was greatly retarded by the introduction of stabilising additives (cyclohexene oxides with cadmium–barium or calcium–zinc carboxylates). The labile chlorine atom in the allyl position was thus detached without formation of a new double bond, so that autocatalytic decomposition reactions did not develop:



p.v.c. model

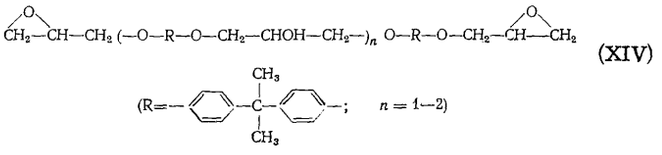


p.v.c. model

(R = CH_3, C_7H_{15})

Furthermore, epoxy-compounds evidently retard chain oxidations by inhibiting breakdown of the intermediate hydroperoxides. The model reaction of t-butyl hydroperoxide with cobalt octanoate shows that a mixture of an epoxide resin and a cadmium soap is more efficient than its components in inhibiting the decomposition of a hydroperoxide. The mixture approaches dibutyltin dilaurate in the efficiency of its action[87,88].

The lower glycidyl ethers have the disadvantages of being volatile and causing dermatitis, so that the non-volatile and less toxic epoxide resins are preferred for stabilising polymers. The glycidyl polyether



(XIV)

obtained by condensing a bisphenol with epichlorohydrin, has been suggested[89] for stabilising vinyl halide polymers.

Polyalkylene glycol ethers RO.[AO]n.R′, where R′ = 2,3-epoxypropyl, A = alkylene (C_6), and n = 2–4, also have a stabilising effect[90]. Dialkyltin epoxysuccinates (n = 1–20) blend well with vinyl halide polymers, do not decompose with the liberation of toxic products when processed, and ensure that compositions should have prolonged thermal stability and good light stability[91].

Products obtained by the reaction of epichlorohydrin with sulphones of formula HO.R.SO_2.R′.OH (R and R′ = C_6H_5 or $C_6H_5CH_2$) have been recommended for stabilising vinyl polymers[92,93]. Epoxidised esters of higher aliphatic acids present in compositions based on poly(vinyl chloride) have not only a stabilising effect but also a plasticising action[94–98]. They are generally used as a secondary stabiliser with magnesium, calcium, and zinc stearates, organotin stabilisers, and phosphites[99–111]. Extremely stable compositions have been obtained by introducing into polyalkenes products of the reaction of polymers containing epoxy-groups with various organic hydroxy- and thio-acids and hydroxyl-containing compounds[112–118].

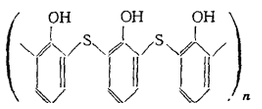
Rubbers modified by furan resins possess enhanced thermal and chemical stability[119].

6. Macromolecular and Oligomeric Sulphur-containing Compounds

Compounds containing sulphur effectively inhibit the thermo-oxidative breakdown of many polymers.

Products obtained by the action of sulphur on atactic polypropylene have been used to stabilise isotactic polypropylene[120–122]. The sulphurised atactic polymer blended well with isotactic polypropylene, was retained in it for a long time, and was not washed out by water. Products of the action of dibenzothiazolyl disulphide (Altax) on atactic polypropylene surpass the sulphurised atactic polymer in their stabilising action[123]. The inhibiting activity of products of the reaction of atactic polypropylene with sulphur or with Altax depends on the period of contact between them. The initial products contain mainly thiol and polysulphide groups, which are converted during the reaction into monosulphide and thioketone groups[124–126]. The greatest stabilising activity is possessed by the initial products, which are as good as certain industrial antioxidants, e.g. isobornylmethylphenol. The high activity of low concentrations of the initial products is due to the rapid conversion of polysulphides into sulphoxides and the involvement of mercapto-groups in chain-terminating reactions. However, thiyl radicals are highly reactive, and are able to initiate oxidation; for this reason the inhibiting activity of the initial products decreases as their concentration increases[127]. If ionol is also added, the thiyl radicals are stabilised, hence secondary initiation is absent, and the efficiency increases[121]. The final products of the interaction of atactic polypropylene with sulphur contain predominantly monosulphide and thioketone groups, which are oxidised to sulphoxides with greater difficulty than is explained by their insignificant stabilising activity[128]. The inhibiting power of the reaction product of polystyrene with sulphur exceeds many times that of sulphurised atactic polypropylene: addition of the former protects polypropylene at 200°C for 110–150 min, whereas the latter guarantees protection for only 7–12 min[129].

Other suggestions for the stabilisation of polyalkenes are a polydisulphide based on decane-1,10-dithiol combined with carbon blacks[130], oligomers obtained by the reaction of phenols with sulphur monochloride or dichloride[131]



(n = 1–4) (XV)

and polyesters based on aliphatic thiodicarboxylic acids mixed with antioxidants of phenolic type [132,133]. Sulphur-containing stabilisers for poly(vinyl chloride) resins are generally used mixed with stabilisers that are acceptors of hydrogen chloride, an example being a mixture of an organic derivative of tin or zinc with a liquid polythiopolythiol

$$HS(CH_2CH_2OCH_2OCH_2CH_2SS)_nCH_2CH_2OCH_2OCH_2CH_2SH \quad (n = 3-6)^{134-136}. \quad \text{(XVI)}$$

The thermo-oxidative degradation of poly(vinyl chloride) resins is presented by polyester condensates of mercapto-alcohols and dicarboxylic acids mixed with lead silicate [137-139].

III. POLYMERS WITH A SYSTEM OF CONJUGATED DOUBLE BONDS

Polymers having systems of conjugated double bonds have recently been proposed as stabilisers for macromolecular compounds. These polymers are able to form relatively inactive biradicals on excitation to a triplet state, and thereby prevent the development of chain decomposition processes in the degradable polymer. The activation energy for the addition of radicals to conjugated polymers is less the lower the energy of excitation of the latter to the triplet state.

Polymers with systems of conjugated double bonds comprise a set of homologous polymers differing in conjugation energy in the transition state, in activation energy, and in energy of excitation. Therefore the use of these conjugated polymers as stabilisers of macromolecular compounds makes it possible in principle to inhibit chain breakdown processes over a wide range of temperatures or energies of exposure. In this connection the use of conjugated polymers is especially promising for raising the limiting operating temperature of known organic and heteroatomic polymers.

Polymers having an acyclic chain of conjugation—polyphenylacetylene, an equimolecular *p*-diethynylbenzene-phenylacetylene copolymer, and dehydrochlorinated poly(vinyl chloride)—inhibit the dehydrochlorination of poly(vinyl chloride) at 175–180°C and retard its breakdown under the influence of ultraviolet radiation. They can be used either independently or mixed with other stabilisers. When polyphenylacetylene is used alone (1 wt.%), the rate of evolution of hydrogen chloride from poly(vinyl chloride) at 175°C diminishes to one-third; the action of polyphenylacetylene is far more effective when mixed with lead silicate [140-142].

Polymers with aromatic rings in the conjugated chain—polyphenylene, polyazophenylene, polyphenyleneaminoquinone—have also been examined as stabilisers for poly(vinyl chloride). Their stabilising action is different from that of polymers having an acyclic conjugated chain. Aromatic conjugated polymers become more effective with rise in temperature, but acyclic conjugated polymers become less effective. The reason for this is that the energy of excitation to the triplet state is higher for polyphenylene than for polyvinylenes; therefore the inhibiting action of the former develops at higher temperatures. The effectiveness of the stabilising action of conjugated polymers is strongly dependent on the conditions of the thermal degradation of poly(vinyl chloride). Comparison of the rates of dehydrochlorination of the latter in nitrogen and in the presence of oxygen shows that aromatic conjugated polymers suppress only the thermo-oxidative degradation of poly(vinyl chloride). This is explained by the greater activity of biradicals of conjugated polymers in reactions with *O*-radicals than in reactions with atomic chlorine and *C*-radicals [143,144].

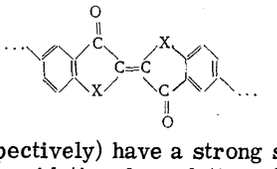
Conjugated polymers—polyphenylene, polyazophenylene, polyphenylacetylene, polydiphenylacetylene—have solved the problem of the thermal stabilisation of three-dimensional polymers based on polyether–acrylates. Addition of a conjugated polymer (5 wt.%) almost completely suppresses the thermo-oxidative degradation of hardened polyether–acrylates at 200°C, without impairing their physicomechanical properties. In the absence of stabilisers 30–35% of the initial polyether–acrylate is degraded under the same conditions [145-148].

Conjugated polymers retard the high-temperature oxidation of polyarylates [149], phenol–formaldehyde resins [150], and polycarbonates [151].

Examination of a large number of conjugated polymer inhibitors reveals that the most active contain in the main conjugation chain heteroatoms with a lone pair of *p*-electrons, such as polyquinonedioxins [152] (Table 1). Polymers having a ladderlike structure—(XX)–(XXIII), (XXV), (XXVI)—as well as polymer (XIX) possess the characteristic properties of conjugated systems: i.e. the *p*-electrons of their heteroatoms are conjugated with the π-electrons of the quinone and aromatic rings. In polymers (XVII), (XVIII), and (XXIV) conjugation is weakly developed, being least in (XVII), for which a tautomeric transition is impossible.

The thermo-oxidative degradation of polycarbonates was conducted at 300°C and an oxygen pressure of 500 mmHg. The efficiency of stabilisers against degradation was determined from the kinetics of the absorption of oxygen and from viscometric measurements in dichloromethane. An industrial polycarbonate may be contaminated with sodium chloride, which accelerates considerably the high-temperature degradation of the polymer (it reacts with terminal phenolic hydroxyls to evolve hydrogen chloride, which catalyses hydrolysis of the ester bonds in the polymer). Polyquinones inhibit degradation of an unpurified polycarbonate. Polymers of ladderlike structure containing two heteroatoms per monomer unit are especially effective; the inhibiting power of linear polymers is considerably lower (Fig. 2). The stabilising effect is strengthened by increasing the addition of polymeric quinones to 2 wt.%. [153-158]

Polymeric colorants such as polyindigo and polythioindigo



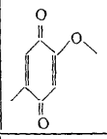
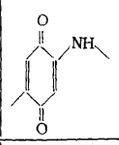
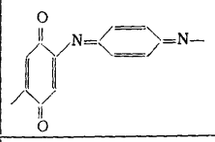
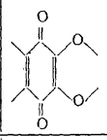
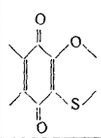
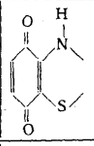
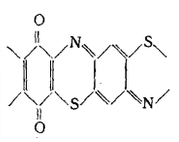
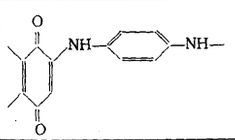
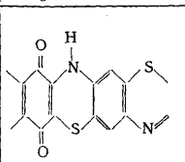
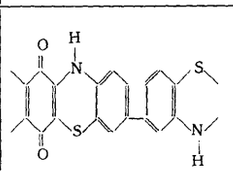
(XXVII)

(X = NH and S respectively) have a strong stabilising effect against the thermo-oxidative degradation of polyamide fibres [159]. When a fibre has been treated with such a dye or an analogue of low molecular weight, not only does its strength not diminish during degradation, but may even increase in some cases. The stabilising effect is most clearly evident in Kapron [6-polyamide] fibre, when the effectiveness diminishes in the sequence

polymeric dyes > lower analogues > Indanthren dyes

This can be attributed to completion of the supermolecular structure of the fibres under the influence of polar compounds deposited on their surface. Furthermore, a polymeric dye containing systems of conjugated bonds acts as an inhibitor of chain oxidation [159].

Table 1. Polyquinones investigated as stabilisers of polycarbonates[152].

Polymer	Monomer unit	Mol. wt.	Terminal groups	E.s.r. signal
(XVII)		1600	Br*	very weak
(XVIII)		1300	NH_2	weak
(XIX)		1400–1700	H, Cl	signal
(XX)		2200–2500	OH, Cl	signal
(XXI)		1800	Br*	signal
(XXII)		1600–1700	—	signal
(XXIII)		1600–1900	H, Cl	signal
(XXIV)		1500–1800	H, NH_2	weak
(XXV)		2000–2300	—	signal
(XXVI)		2000–2200	—	signal

*Branched chain.

Berlin considers that paramagnetic centres of polyconjugated systems play an activating part in the thermooxidative degradation of polymers (local activation effect).

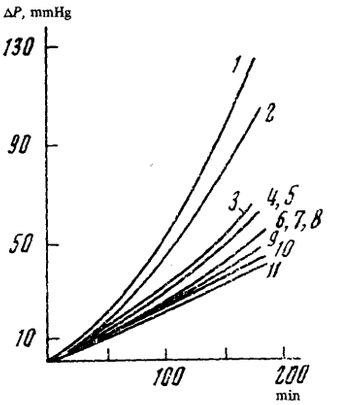


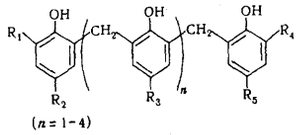
Figure 2. Rate of fall of pressure in the thermo-oxidative degradation of an unpurified polycarbonate in the presence of polymeric stabilisers (1 wt.%)[152]: 1) no addition; 2) (XIX); 3) (XXI); 4) (XXIII); 5) (XVIII); 6) (XVII); 7) (XX); 8) (XXIV); 9) (XXV); 10) (XXII); 11) (XXVI).

At high temperatures the diamagnetic conjugated polymer molecules undergo oxidative dehydropolycondensation, with an increase in their degree of conjugation and denser packing of the molecules in aggregates. This favours excitation of the diamagnetic molecules to the biradical state under the influence of the paramagnetic centres of the conjugated polymer, with the subsequent formation of charge-transfer complexes with peroxy-radicals. Further reactions of the complexes lead to the appearance of inactive products[160–166].

IV. MACROMOLECULAR AND OLIGOMERIC ANALOGUES OF STERICALLY HINDERED PHENOLS

Antioxidants of phenolic type have been widely used in industry because of their great effectiveness and the absence of toxicity[167]. They have the advantage of not discolouring the stabilised polymer. The mechanism of their action has now been studied quite thoroughly. Various sterically hindered phenols have been prepared and examined. Their effectiveness depends on several factors —including the nature of nuclear substituents and their bulk, the ease of free-radical detachment of hydrogen from the phenolic hydroxyl and the stability of the resulting phenoxyl radicals, as well as certain other factors—an aspect which has been reviewed in some detail[1,168–170]. The oxidation products of phenolic antioxidants also possess inhibiting properties, though less pronounced than those of the original phenols[171,172].

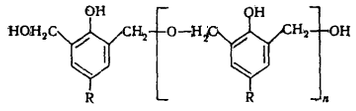
While exhibiting all the valuable features of phenolic stabilisers of low molecular weight, the polymeric analogues of sterically hindered phenols are considerably less volatile and soluble. Polyphenols of formula



(XXVIII)

($n = 1-4$)

(R^1–R^5 = alkyls and $n = 1-4$) have been prepared and found to be effective antioxidants for polyalkenes[173]. The phenolic polycondensate may consist of various aromatic monomer units—isopropylidene-*pp'*-diphenolic, s-butylidene-*pp'*-diphenolic, bisphenol sulphone, bisphenol sulphoxide, etc.—joined together by methylene, ethylene, ethylidene, di-isopropenylbenzene, and other groups[174–180]. A synergetic effect is observed when polyphenols are used mixed with bisdodecyl or bisoctadecyl thiodipropionate[181]. Polyhydroxyphenylalkanes also are effective antioxidants. Polypropylene has been stabilised with a mixture of a polyhydroxyphenylalkane (2,2,5,5-tetrakis-*p*-hydroxyphenylhexane) and bisoctadecyl thiodipropionate: the time at 140°C before darkening occurred was 180 h, but in the absence of a stabiliser 24 h.[182] Phenol–formaldehyde oligomers have been used to stabilise polyether-urethanes[183] and poly(vinyl chloride).[184] A method of stabilising poly(vinyl chloride) towards light and heat uses mixtures of a polyoxybenzyl ether



(XXIX)

($n > 1$; R = CH_3, $C(CH_3)_3$, C_6H_5, etc.) or a polyoxybenzyl alcohol with lead stearate or silicate as acceptor of hydrogen chloride. These inhibitors blend well with poly(vinyl chloride). The thermal stability of the latter is trebled by adding the polyoxybenzyl ether (1 wt.%).[185,186]

V. MACROMOLECULAR AND OLIGOMERIC ANALOGUES OF BENZOPHENONE

Derivatives of hydroxybenzophenone are widely used for the photostabilisation of polymers. Apart from the light-filtering effect, the decisive process with benzophenone derivatives is the resonance dipole–dipole interaction, leading to a radiationless transfer of the electronic excitation energy from the polymer to the photostabiliser[187–190].

Polymeric and oligomeric analogues of benzophenone have been proposed for protecting polymers from ultraviolet radiation. Polyalkenes and poly(vinyl chloride) resins have been stabilised with homopolymers of 2-hydroxy-4-methacryloylbenzophenone and 2-hydroxy-4-(meth)acryloylacetophenone. Poly(vinyl chloride) film yellowed and cracked after exposure to ultraviolet radiation for 200 h, but a film stabilised with poly-4-acryloyl-2-hydroxybenzophenone remained for 600 h without change. The photostability of poly(butyl acrylate) improved in the presence of poly-2-hydroxy-4-methacryloyl-5-t-butylbenzophenone[191]. Polymers of 2-hydroxy-4-(2-hydroxy-3-methacryloylpropoxy)benzophenone (XXX), 4-(3-acryloyl-2-hydroxypropoxy)-2,2'-dihydroxybenzophenone, etc.[192] and also the copolymer of (XXX) with phenyl 2-hydroxy-5-methacryloylmethoxybenzoate[193] have been recommended for the photostabilisation of a copolymer of vinylidene chloride with ethyl acrylate.

The homopolymers of acrylic and methacrylic derivatives of 4-alkoxy-2-hydroxybenzophenones have been used for the photostabilisation of polystyrene, poly(vinyl chloride), poly(methyl methacrylate), etc. Fig. 3 shows that poly(benzophenone acrylate) is more effective than the corresponding methacrylate as a photostabiliser for polystyrene, which is explained by the better compatibility of the former with the polymer. A copolymer of styrene with benzophenone methacrylate and a mixture of polystyrene with poly(benzophenone acrylate) have roughly the same stability towards light. Poly(benzophenone methacrylate) is an effective photostabiliser of poly(vinyl chloride) (Fig. 4).[194]

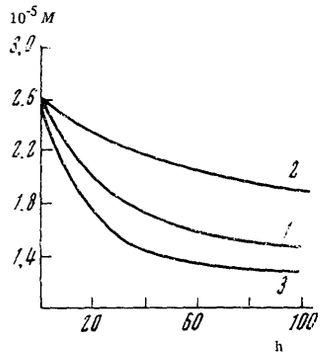


Figure 3. Dependence of molecular weight of polystyrene on time of illumination in the presence of polymeric stabilisers[194]: 1) poly(benzophenone methacrylate); 2) poly(benzophenone acrylate); 3) control specimen.

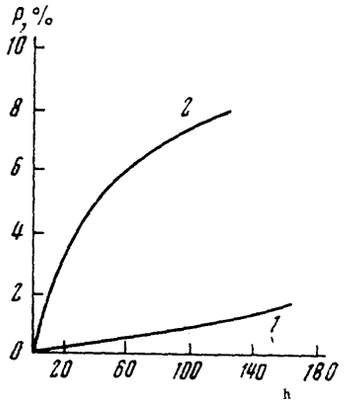
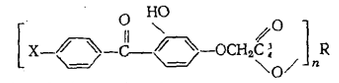


Figure 4. Dependence of content of gel fraction on time of irradiation of poly(vinyl chloride)[194]: 1) with added poly(benzophenone methacrylate); 2) no addition.

Oligomeric hydroxylated polyesters

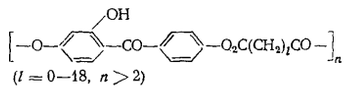


(XXXI)

(where X = H, AlkO (C_{1-4}), R = residue of aliphatic (C_{2-10}) polyhydric alcohol with n = 2–6 OH) have been

recommended as light-protective additives, which are well preserved in the polymer. They were obtained by reaction between 4-benzoyl-3-hydroxyphenoxyacetic acid and a polyhydric alcohol (ethane-1,2-diol, n-decane-1,10-diol, etc.). Tests in air for 10 weeks showed that the polymeric stabiliser was completely preserved in films, whereas the concentration of hydroxybenzophenones diminished considerably [195].

Products of the condensation of 2,4,4′-trihydroxybenzophenone with dicarboxylic acids (succinic, glutaric, adipic) or with their acid halides



(XXXII)

($l = 0$—18, $n > 2$)

have been proposed as photostabilisers which are well preserved in polyalkenes [196].

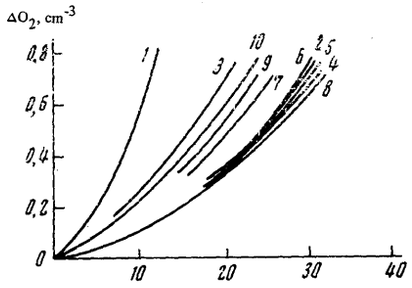
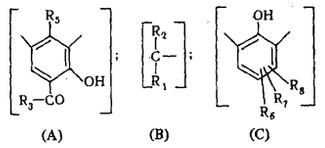


Figure 5. Photo-oxidation of stabilised polypropylene films at 60°C (distance from lamp to film 7 mm, with 2—mm Pyrex filter) with different stabilisers (0.0184 mole kg^{-1}): [197] 1) no additive; 2) 2-hydroxy-4-octyloxybenzophenone; 3) as (2) after extraction; 4) condensate (XXXIV); 5) as (4) after extraction; 6) condensate (XXXIII); 7) as (6) after extraction; 8) condensate (XXXV) before and after extraction; 9) condensate (XXXVI); 10) as (9) after extraction.

Polypropylene stabilised with various polycondensates—of 2-hydroxy-4,4′-bis-β-hydroxyethoxybenzophenone with thio-ββ′-dipropionic acid (XXXIII), 2,4,4′-trihydroxybenzophenone with a mixture of thio-ββ′-dipropionic (0.7 mole) and isophthalic (0.3 mole) acids (XXXIV), 2,2′-dihydroxy-4,4′-β-hydroxyethoxybenzophenone with thio-ββ′-dipropionic acid (XXXV), and 2,2′,4,4′-tetrahydroxybenzophenone with a mixture of isophthalic (0.7 mole) and adipic (0.3 mole) acids (XXXVI)—has been subjected to photodegradation before and after extraction with chlorinated hydrocarbons [197]. Fig. 5 shows that photo-oxidation is appreciably affected by extraction only with the relatively simple stabiliser 2-hydroxy-4-octyloxybenzophenone (curves *2* and *3*). The polycondensation product (XXXIII) is also partly extracted from polypropylene (curves *6* and *7*). The remaining stabilisers are almost unaffected by extraction. The most effective are polycondensates containing thio-ββ′-dipropionic acid—(XXXIV) and (XXXV)—probably because sulphur-containing groups are involved in the breakdown of hydroperoxides [198] formed during irradiation in air.

Halogenated polyalkenes have been stabilised by introducing an oligomeric product (M = 500) of the reaction of formaldehyde (or benzaldehyde) with *o*-hydroxybenzophenone (or acetophenone). The product absorbed intensely in the ultraviolet (340 nm) and exhibited high stabilising activity [199,200].

Polycondensates [201–203] with $M \geqslant 400$ and consisting of the units



(XXXVII)

(where R^1 and R^2 = H, Alk (C_{1-6}), chloroalkyl, furyl, vinyl, propenyl, phenyl; R^3 = Alk (C_{1-6}), Ar; R^4 and R^5 = H, OH, Hal, AlkO, Alk; and R^6, R^7, R^8 = H, OH, Hal, Ar, ArO, cycloalkyl) stabilise vinyl polymers towards heat and light. The molar proportions of the components are 1 : 2 : 1. Table 2 gives the test results.

Table 2. Stability of vinyl polymers containing added polycondensates towards heat and light [201].

Initial components of polymeric stabiliser			Polymer	Thermal stability*	Ultraviolet stability**
I	II	III			
o-Hydroxyacetophenone	formaldehyde	dodecylphenol	polypropylene	not discoloured	5
2-Hydroxy-4,6-dimethylbenzophenone	acetone	*m*-butylphenol	polyethylene	not discoloured	3
2,4-Dihydroxybenzophenone	furaldehyde	octadecylphenol	polyethylene	not discoloured	4
4-Chloro-2-hydroxybenzophenone	butyraldehyde	3,5-dichloro-4-methylphenol	poly(vinyl chloride)	discoloured	3
2-Hydroxy-4-methoxybenzophenone	benzaldehyde	octylphenol	ethylene–ethyl acrylate copolymer	not discoloured	3
o-Hydroxybenzophenone	formaldehyde	phenol	poly(vinyl fluoride)	not discoloured	4

*Under the test conditions (210°C for 30 min) the control specimen—the polymer without a stabiliser—is discoloured.

**The ratio of the time for the stabilised film to disintegrate to the corresponding time for the control film.

Macromolecular analogues of *o*-hydroxybenzophenone, obtained by the Fries rearrangement of polyarylates, have been proposed for the photostabilisation of various vinyl polymers [204]. The polymeric stabilisers possess low volatility, blend well with many polymers, and are as good as *o*-hydroxybenzophenone in effectiveness. Comparison of the infrared spectra of samples of poly(vinyl fluoride) film containing 1–2 wt.% of such a polyketone before and after being heated in a vacuum (0.1 mmHg) at 100°C for 3 h showed hardly any change in the content of polymeric stabilisers in the film, whereas the content of *o*-hydroxybenzophenone in a control specimen had decreased significantly. The effectiveness of the polymeric stabilisers was maintained even after exposure of the film at 60°C to ultraviolet radiation for 2 months.

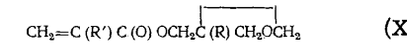
VI. OTHER MACROMOLECULAR AND OLIGOMERIC COMPOUNDS

Various macromolecular compounds containing an open chain of carbon atoms have been suggested for stabilising polymers. Macromolecular hydrocarbons, alcohols, acids and their salts, esters, ethers, etc. have found application.

Thermal stabilisation of poly(vinyl halide) resins has been effected by additions of polyethylene (0.5–2.0 wt.%),[205,206] which eliminated charring or any decomposition of the material during processing. The stabilising effect of polyethylene is explained, in the Reviewers' opinion, by two factors. Polyethylene is able to combine with atomic chlorine formed in the thermal degradation of poly(vinyl chloride), thus preventing development of free-radical degradation processes in the polymer and in the corresponding segments of vinyl chloride copolymers[1]. Such explanation seems probable, since polyalkenes are easily chlorinated at ~150°C even in the dark[207]. On the other hand, hydrogen chloride catalyses the thermal breakdown of poly(vinyl chloride).[208–211] It has been shown recently that the thickness of the specimen has a great influence on the rate of breakdown of this polymer. There exists a critical size, beyond which the elimination of hydrogen chloride becomes autocatalytic[212]. This indicates that polyethylene acts as a stabiliser also by diminishing the contact between hydrogen chloride and the polymer macromolecules, diminishing the relative importance of autocatalytic processes in the polymer degradation, and hence decreasing the overall rate of breakdown. Polyalkenes also stabilise polyoxymethylene. Its thermal stability is improved by polybutene and by an ethylene–vinyl acetate copolymer[213,214]; polyethylene and polypropylene are less efficient in stabilising polyoxymethylene. Oligomeric polyphenylenes—derivatives of toluene, *o*-, *m*-, and *p*-xylene, etc.—show promise for the thermal stabilisation of isotactic polypropylene. The effectiveness of these stabilisers is greatly increased by the addition of bisdodecyl thiodipropionate[215].

A polyol (a polyethylene glycol) has been used[216] in combination with sodium tellurite or selenite to improve the thermal stability and the transparency of poly(vinyl chloride). Polymers containing nitrile groups are stabilised by the addition of a polyhydric alcohol based on polyoxypropylene having a hydroxyl number of 60–700 and molecular weight 400–3000.[217]

A linear acrylic ternary polymer (M = 150 000 to 2 000 000), comprising monomer units of methyl methacrylate, ethyl acrylate, and an ester of an alkoxy-acid of formula



(XXXVIII)

(where R = Alk (C_{1-4}) and R′ = H, CH_3) stabilises poly(vinyl chloride) of intermediate or high molecular weight[218]. Pure poly(methyl methacrylate) has no effect on the rate of breakdown of poly(vinyl chloride).[219]

The introduction of oligoether–acrylate segments into the poly(methyl methacrylate) chain improves its physico-mechanical properties and enhances the thermal stability[220].

The polymeric salt obtained by the reaction of a copolymer of styrene and maleic anhydride with ammonium hydroxide protects poly(vinylidene chloride) from the action of ultraviolet rays[221].

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