New developments in speciality polymers: polymeric stabilizers*

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Many new speciality polymers have been developed in the last few years. In this paper polymeric stabilizers (antioxidants, flame retardants and ultraviolet stabilizers) will be discussed. Polymeric antioxidants of the hindered-phenol type, copolymers of 2,6-ditertiarybutyl-4-vinyl(or isopropenyl)phenol with styrene, methyl methacrylate, or more importantly butadiene or isoprene have been prepared; hydrogenation of the latter copolymers gave copolymers of the two polymerizable phenolic antioxidants with ethylene or ethylene/propylene. The polymeric antioxidants have been blended with diene polymers and selected polyolefins and have improved the long-term oxidative stability of these polymers. Polymeric flame retardants have been prepared by copolymerizing styrene and/or acrylonitrile with acrylates and methacrylates of aliphatic bromine-containing alcohols or bromine-containing phenols. Polymers with polymer-bound flame retardants have a higher limiting oxygen index compared with the original polymer. A new class of polymerizable ultraviolet stabilizers has also been developed; these stabilizers are styryl, α-methylstyryl, acryloyl and methacryloyl derivatives of 2(2-hydroxyphenyl)2H-benzotriazoles. These monomers have been copolymerized with styrene, acrylates and methacrylates. 2(2-Hydroxyphenyl)2H-benzotriazoles substituted in the 4 position of the benzotriazole ring with hydroxyl, acetoxy or carboxyl groups suitable for incorporation into polyesters, polycarbonates, polyamides and epoxy resins have also been synthesized. All 2(2-hydroxyphenyl)2H-benzotriazole ultraviolet absorbers and the polymers into which they are incorporated have high light absorbency with λ_{max} between 330 and 350 nm and extinction coefficients in some cases as high as 4.5×10^4 l mol^{-1} cm^{-1}.

(Keywords: polymeric stabilizers; antioxidants; flame retardants; ultraviolet stabilizers; increased service life; long term stability)

The Symposium on 'Speciality Polymers' was held at an appropiate time because it was at the beginning of a period when the commercial development and use of speciality polymers have started to have a tremendous impact on the development of polymer science. Speciality polymers are made and used for specific combinations of properties, often without the normal primary objective of low price[1]. Speciality polymers are 'tailor made' with a specific combination of properties to fill specific and predetermined needs; their properties make them uniquely suited for the intended use. Scientifically speaking, most speciality polymers are functional polymers.

If we had looked about 10 years ago at the status of polymer science as reflected in its industrial development, we would have drawn a curve such as the one shown in *Figure 1*[2] with much of the emphasis on the maximization of properties per unit price in commodity polymers. The volume of plastics production plateaued at $2-4 \times 10^8$ tons per year, depending on the market in underdeveloped countries (the developed countries currently use about 100 kg/person/year plastic materials and less than a quarter of the world's population has reached that development level) and on the availability of the primary raw material oil[3]. A decade ago there was very little

general recognition that the next growth period in plastics would not be in the commodity plastics field. Even though this field is still expanding, work on highly sophisticated speciality polymers is clearly the thrust of research in the near future. This surge requires highly sophisticated scientists who will have to be properly trained and prepared in all phases of polymer science and technology to accomplish this task.

Polymer science and technology has developed over the years into the subdisciplines of polymer chemistry,
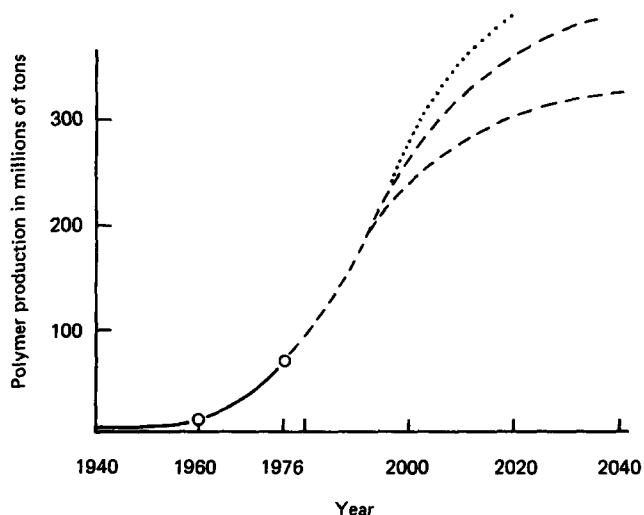

Figure 1 Worldwide polymer production (million tons as a function of time)

Chemistry

Life sciences

Polymer

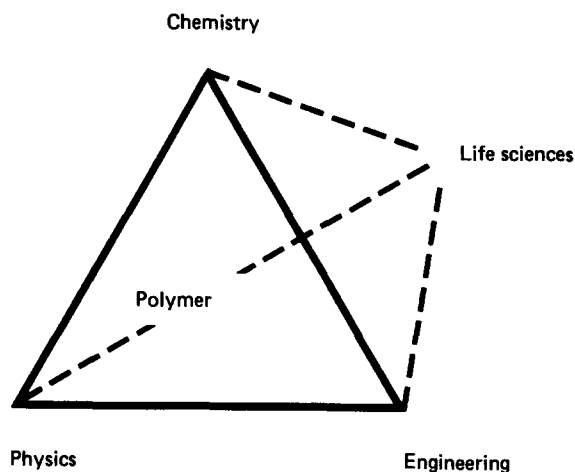Physics   Engineering

Figure 2 Ten years ago, the next thrust in the development of polymer science and technology is expected to be the interaction with the life sciences

Polymer Science Development

Functional polymers

Polymer engineering

Polymer physics

Polymer chemistry
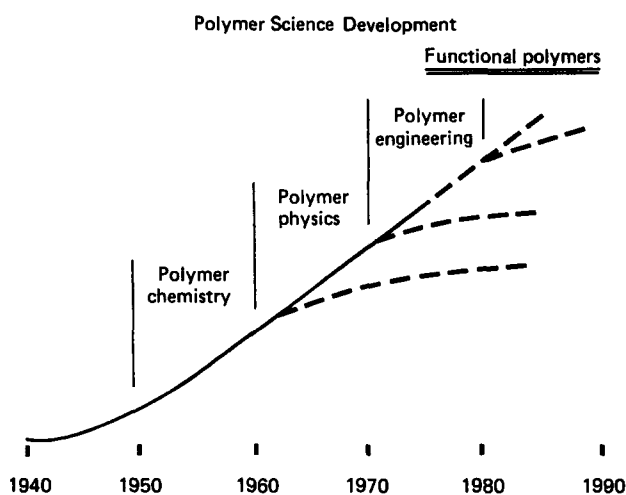
1940   1950   1960   1970   1980   1990

Figure 3 Polymer science, as other sciences, has developed in epochs, and the ideas and breakthroughs came clustered in individual subdisciplines

physics and engineering, each discipline being an integral and essential part of the development of plastic materials with optimum properties and at an economic price. About 10 years ago it was proposed (see *Figure 2*) that the next thrust in the development of polymer science and technology would be the interaction with the life sciences, especially medicine, agriculture and the production and preservation of food and energy. Many of these predictions have come true.

Polymer science, as other sciences, has developed in epochs, and the ideas and breakthroughs came clustered in individual subdisciplines (*Figure 3*). It has been said that polymer chemistry had produced most of the advancement in research in the 1950s, polymer physics in the 1960s, and polymer engineering in the 1970s. It was also proposed that the 1980s would be the era of functional polymers, or, from the application point of view, the era of speciality polymers. This thrust of a 'return to chemistry' in a highly sophisticated way involved polymer chemistry with a full understanding of polymer physics, polymer engineering and application. If we look back further, we may recognize that much of the early development of polymer science, for example in the 1940s, was based on polymer physical chemistry, a forerunner of engineering.

Next year, a symposium entitled 'Polymer Science in the Next Decade' is planned to look into the prospects for polymer science in the 1990s and towards the turn of the century.

One can speculate on how polymer science has developed in a somewhat cyclical pattern by using the helical structure of polypropylene as the model. Several years ago at the dedication of the Research Center of Montedison in Ferrara, Italy, a stainless steel model of polypropylene was erected depicting the helix of polypropylene on an enlarged scale of about 4×10^9 (*Figure 4*). We could visualize the return of polymer chemistry at a more sophisticated level by one turn of the helix and three monomer units.

INTRODUCTION

Many polymers with functional groups are now being synthesized, tested and used, not only for their macromolecular properties (the bulk properties of the polymers) but also for the properties of the functional groups. Some functional groups may give the polymers chemical reactivity, spectral or biological/medicinal properties; they may be photothermally or biologically active; they may be useful as drugs, catalysts, antioxidants, flame retardants or u.v. absorbers. Functional groups may be permanently attached to the polymer chain or they may only be temporarily attached, to be removed by degradation or hydrolysis when needed; in such cases, the low molecular weight groups released may then be responsible for the activity[4].

Improved polymer properties or polymers with bulk properties of higher sophistication are also needed for commodity polymers, such as moulding engineering plastics; high-temperature, high-performance polymers; high-temperature, low-friction polymers (fluorocarbon resins); or polymers with high-temperature, low glass transition temperature characteristics (silicones). New
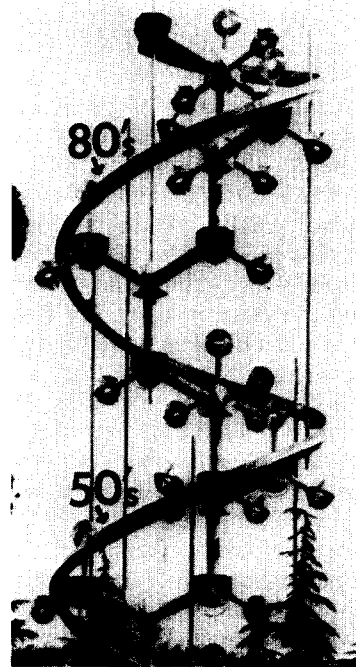

Figure 4 Stainless steel model of polypropylene helix outside Montedison Research Center, Ferrara, Italy (enlarged scale of about 4×10^9)

polymers are also being developed for special applications in consumer products. Special polymers are being developed to replace metals or for use in metal/polymer interfaces. Speciality polymers, primarily functional synthetic polymers, are being sought for applications in agriculture, medicine, food and nutrition, generation and preservation of energy (tertiary oil recovery, solar energy), for various aspects of handling, storage and retrieval of information, for electrical, electronic and optical applications and for use in pharmacy and medicine.

In the energy field, for example, enhanced oil recovery requires polymers with special structural design to provide the properties needed for the requirements of the individual oil fields. Solar energy is considered the ultimate source of energy and polymeric materials used in equipment for collecting solar energy must be photostabilized by polymer-bound photostabilizers and/or antioxidants. Effective polymer-bound stabilizers are also needed in space, where the loss of stabilizer at the low pressure of space cannot be tolerated.

POLYMERIZABLE AND POLYMERIC ANTIOXIDANTS

The idea of having antioxidants permanently bound to a polymer, in particular to protect unsaturated elastomers, has been known for some time[5]. Although the principle, that polymer-bound antioxidants provide effective long-term stability for polymers, is now established, its application is still not in general use nor is the general principle fully accepted. Recently, Scott has demonstrated that certain hindered phenol antioxidants can be bound onto polymers by radical reactions or during vulcanization[6-8]. Thiol groups or bromine atoms, when separated with a short flexible spacer group from the antioxidant part of the molecule, provide the reactive group for this reaction. Using this technique, phenolic antioxidants or other antioxidant groups such as molecules with aromatic amine groups could be incorporated into unsaturated polymers. Since this reaction is usually not quantitative, some unreacted, low molecular weight antioxidant is left in the resins, which is believed to add to the stabilizing action of the polymer-bound antioxidant.

In our general approach of preparing permanent polymerizable or polymer-bound antioxidants, we have undertaken the synthesis of 2,6-ditertiary-butyl-4-vinylphenol (DBVP) and 2,6-ditertiarybutyl-4-isopropenyphenol (DBPP). These monomers and their polymers were first prepared by Braun[9], who studied the radicals obtained by oxidation of the monomers and their polymers using e.s.r. spectroscopy. We have synthesized the two compounds, DBVP and DBPP, by an improved and very simple route[10,11]. Acetylation of 2,6-ditertiary-butyl-phenol, reduction of the carbonyl function of the acetyl group to the carbinol, and dehydration gave DBVP. Reaction of 2,6-ditertiarybutyl-4-acetylphenol with methyl magnesium iodide followed by dehydration of the tertiary carbinol gave DBPP. DBVP and DBPP were copolymerized with styrene and methyl methacrylate to copolymers with varied comonomer compositions; most importantly, however, DBVP and DBPP could be polymerized with butadiene and isoprene in emulsion with water-soluble azo initiators (equation (1)). These diene copolymers contain 6–10 mol% of DBVP and DBPP in the polymer equation (1).

Equation (1)

Co-hexanoate/Et₃Al
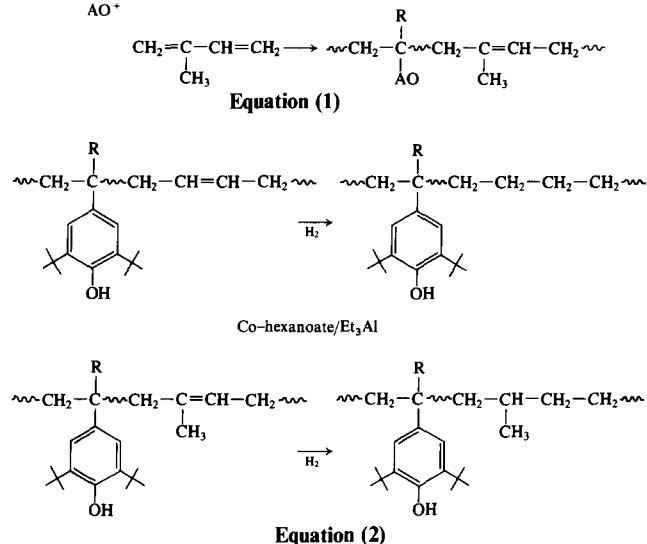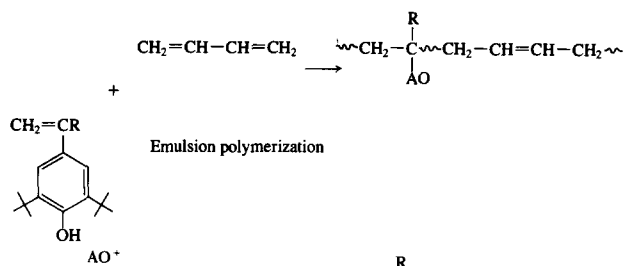
Equation (2)

All four copolymers were hydrogenated catalytically with cobalt hexanoate/triethylaluminium catalysts to the copolymers of DBVP and DBPP ethylene/propylene alternating copolymers (from the isoprene copolymers) (equation (2)).

The hydrogenation of the butadiene copolymers required $\approx 5-10$ mol% of the hydrogenation catalyst, while the copolymers of isoprene required as much as $10-20$ mol% of the reduced cobalt hexanoate hydrogenation catalyst. The hydrogenation was carried out at a temperature slightly higher than room temperature and at a relatively modest hydrogen pressure, 5–10 atm[12].

The eight polymers of DBVP and DBPP prepared from butadiene and isoprene by emulsion polymerization had molecular weights of $\approx 30\,000-50\,000$. They, and the hydrogenated polymers were tested as polymeric antioxidants with several polymers. Since the polymeric antioxidants had ≈ 6 mol% of DBVP or DBPP in the polymer, and a commonly used concentration of phenolic antioxidants for the stabilization of polyolefins is ≈ 0.1–0.2%, our polymeric antioxidants (2wt%) were blended with the polymers which were the target of stabilization. The copolymers of DBVP and DBPP with butadiene were blended with polybutadiene. The copolymers of DBVP and DBPP with isoprene were blended with polyisoprene. The hydrogenated copolymers of butadiene with DBVP or DBPP were blended with low-density, high-pressure polyethylene and low-density, low-pressure polyethylene and the hydrogenated copolymer of isoprene, and DBVP and DBPP were blended with polypropylene. The antioxidant effectiveness of these copolymers was studied by investigating the oxygen uptake of the polymer blends in the melt at 150° C.

In all cases it could be shown that the polymeric antioxidants were more effective for long-term stabilization of the polyolefins, compared with unstabilized polymers or polymers stabilized with low moleceular weight antioxidants. In some cases, the induction periods

of oxygen uptake were slightly longer with high molecular weight antioxidants than with low molecular weight antioxidants; our studies are, however, preliminary and more detailed work must be carried out to ascertain beyond any doubt the higher effectiveness of polymeric antioxidants for long-term protection of polymers against autooxidation.

POLYMERICABLE AND POLYMERIC FLAME RETARDANTS

Flame retardants of high molecular weights have been used in the past and some of them, particularly those with phosphorous in the molecule, have been found effective.

We have studied the use of bromine-containing polymerizable flame retardants and have investigated acrylates and methacrylates of brominated alcohols and phenols. The monomers were synthesized, characterized and their polymerizability established. The polymers were investigated for their thermal stability and limiting oxygen index (LOI).

The acrylates and methacrylates of 2,3-dibromopropanol, 2,4,6-tribromophenol, and pentabromophenol were synthesized (equation (3))[13-16]. These compounds

Equation (3)
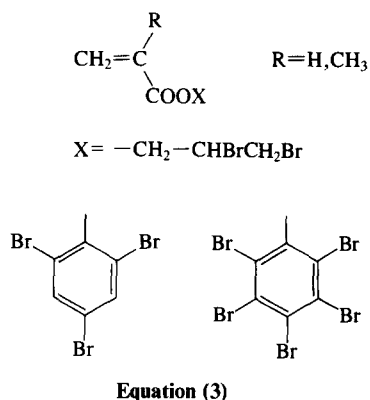
allowed a comparison of acrylates and methacrylates of aliphatic bromine-containing units with those containing aromatic bromine in the molecule. As an additional test of the effectiveness of these polymeric flame retardants, the thermal stability of the polymers containing these units was investigated.

To be able to explain the effectiveness of the flame retardant monomers, a careful determination of the copolymerization and terpolymerization parameters of the six flame-retardant monomers was carried out. The monomers were studied in copolymerizations with styrene (equation (4)), and in terpolymerization with styrene

Equation (4)
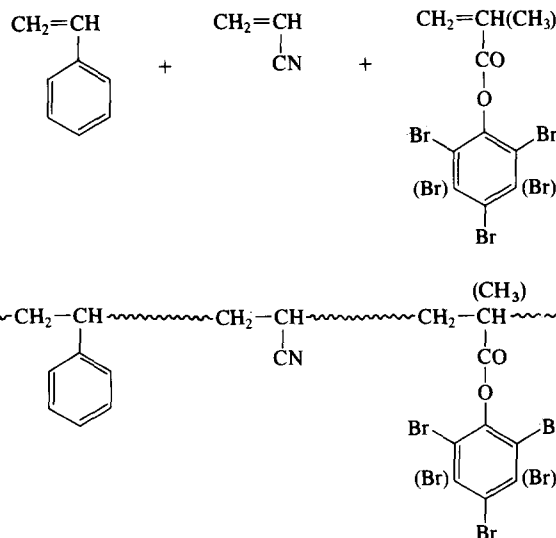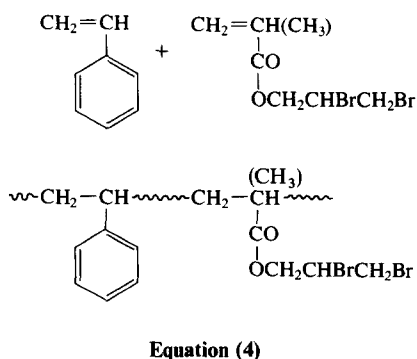
Equation (5)

and acrylonitrile (equation (5)). Co- and terpolymerizations were readily accomplished in emulsion or in dimethylformamide solutions. From our experiments it can be concluded that the LOI of the polymers containing polymer-bound flame retardants is increased from 0.18 for the unstabilized polymers to 0.26 with ≈ 5 mol% of aromatic bromine-containing monomers and up to nearly 0.30 with aliphatic bromine-containing comonomers. When the thermal stability of the copolymers was studied, it became clear that the stability of the polymers with polymerized flame retardants in the chain, especially those that had methacrylate-methacrylate linkages, was lower. The maximum degradation rate by differential thermogravimetry was at $\approx 300°C$ (measured at a rate of $10°C$ min^{-1} temperature increase). The styrene-methacrylate or -acrylate linkages had a maximum degradation rate temperature of nearly 350°C. When acrylonitrile was the termonomer, the maximum degradation rate temperature increased to nearly 400°C.

In our studies on polymeric flame retardants, we have shown that various polymerizable acrylates and methacrylates of bromine-containing phenols or alcohols increased the LOI to a level where the flammability of the total polymer was low enough to make it acceptable. In cases of special co- or terpolymers where the links of the individual comonomers are unfavourable, a decrease in the thermal stability of the polymers was observed.

POLYMERIZABLE AND POLYMERIC U.V. STABILIZERS

When used outside, or indoors under u.v. light, plastic materials must be stabilized against u.v. radiation by u.v. stabilizers[17]. Several categories of such stabilizers are used which include u.v. screens, quenchers and hydroperoxide decomposers (2,2,6,6-tetramethylpiperidine derivatives) (HALS). The most frequently used u.v. stabilizers are u.v. screens, molecules which preferentially absorb the damaging u.v. radiation and are capable of returning essentially quantitively to the ground state, converting the energy of the photon to vibrational energy.

Over the years, a number of polymerizable u.v. stabilizers have been developed. They include such classes as salicylates[18,20], 2-hydroxybenzophenones[21], α-cyano-β-phenylcinnamates[22] and, most recently, 2(2-hydroxyphenyl)2H-benzotriazoles[23,24] (equation (6)).

Equation (6)

Equation (7)
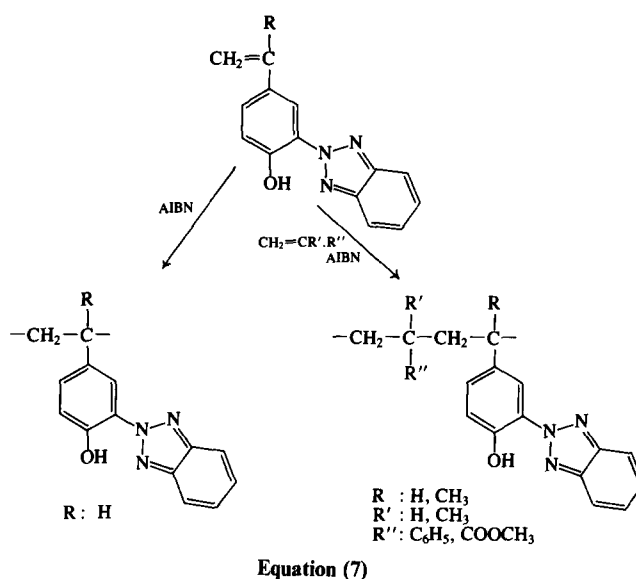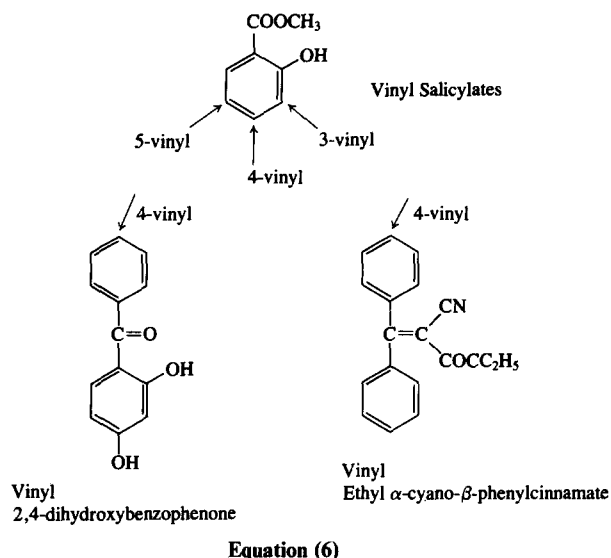
Most effective stabilizers have a hydroxyl group in a position *ortho* to the other functional group on an aromatic ring. Structures of excited states (coplanar structures with positive and negative charges) similar to those described for the *ortho*-hydroxybenzophenones also seem to be effective for 2(2-hydroxyphenyl)2H-benzotriazole u.v. stabilizers. It appears that in the excited state of these types of compounds coplanarity is achieved by hydrogen bonding of the hydroxyl group to the nitrogen 1 or 3 of the triazole ring, and charged species are involved in the energy dissipation in 2(2-hydroxyphenyl)2H-benzotriazoles, similar to the structures which have been demonstrated for the *ortho*-hydroxybenzophenones.

The myth that u.v. stabilizers or stabilizers in general *must* have relatively high mobility in the polymer matrix to be effective has, however, persisted until recently.

In the last two to five years there has been increasing demand for the development of polymeric u.v. stabilizers or polymerizable stabilizers that could be used for incorporation into polymers[25]. The early work on u.v. stabilizers was, however, not successful because in the first attempts methacrylate-type stabilizers were chosen to be incorporated into polyolefins[26].

We have pursued the synthesis of monomeric, oligomeric and polymeric u.v. stabilizers since the early 1970s. Initially, we prepared three isomeric vinyl salicylates[18][20], 4-vinyl-2',4'-dihydroxybenzophenones[21], and α-cyano-β-phenylcinnamates[22], and have studied their u.v. behaviour and their polymerization and copolymerization. In the last five years we have intensively worked on the preparation of polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles.

In general, functional groups can be introduced into polymers by polymer reactions or by the preparation of a functionally substituted monomer which can then be incorporated into the polymer by copolymerization or grafting.

With the aim of preparing 2(2-hydroxyphenyl)2H-benzotriazoles, we have chosen to prepare styrene derivatives (with a vinyl or isopropenyl group directly attached to the phenyl group of the stabilizer[23]) or acrylates or methacrylates of 2(2-hydroxyphenyl)2H-benzotriazoles[28]. These monomers could be polymerized with acrylic- or styrene-type monomers; excellent incorporation of these monomers into the polymers (equation (7)) was achieved.

The most important class of u.v. screens used as stabilizers are 2(2-hydroxyphenyl)2H-benzotriazoles. Since the early work on benzotriazoles by Elb[29][30], a large number of 2(2-hydroxyphenyl)2H-benzotriazoles have been synthesized. In the 1950s these compounds were recognized as very effective u.v. stabilizers, and their initial photochemistry was investigated[31].

In the early work on 2(2-hydroxyphenyl)2H-benzotriazoles[32][34], some polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles had been prepared. These compounds had the polymerizable group attached to the hydroxy group which was placed in the 4 position of the benzotriazole ring; acrylamides, vinyl sulphones, and other compounds with polymerizable groups were prepared. However, little work was carried out on the polymerization of these compounds and the properties of the polymers, especially their photophysical behaviour. At about the same time, a number of nonpolymerizable 2(2-hydroxyphenyl)2H-benzotriazoles such as 2(2-hydroxy-5-methylphenyl)2H-benzotriazoles were synthesized and ultimately commercialized.

We have carried out an extensive study of the synthesis of new and unusual 2(2-hydroxyphenyl)2H-benzotriazoles. The work has been divided into several areas: the synthesis of (a) 2[2-hydroxy-5-vinyl(isopropenyl)phenyl]2H-benzotriazole[24][35], 2(2-hydroxy-methylphenyl(2H-5-vinylbenzotriazoles[36], and the grafting of 2[2-hydroxy-5-vinyl(isopropenyl)phenyl]2H-benzotriazoles onto polybutadienes[37] and other polymers[38]; (b) u.v. absorbers of the 2(2-hydroxyphenyl)2H-benzotriazole family with more than two benzotriazole groups in the molecule[39]; (c) polymerizable acrylate and methacrylate u.v. absorbers with more than one benzotriazole ring in the molecule[40]; (d) u.v. absorbers with both benzotriazole and benzophenone groups in the molecule[41]; (e) u.v. absorbers with more than one polymerizable hydroxyl group and having two benzotriazole rings in the molecule[42], and (f) vinyl and isopropenyl monomers (styryl or α-methylstyryl derivatives) of u.v. absorbers with more than two 2(2-hydroxyphenyl)2H-benzotriazoles in the molecule[43]. We have completed most of our synthetic objectives and part of the study of the application of these materials.

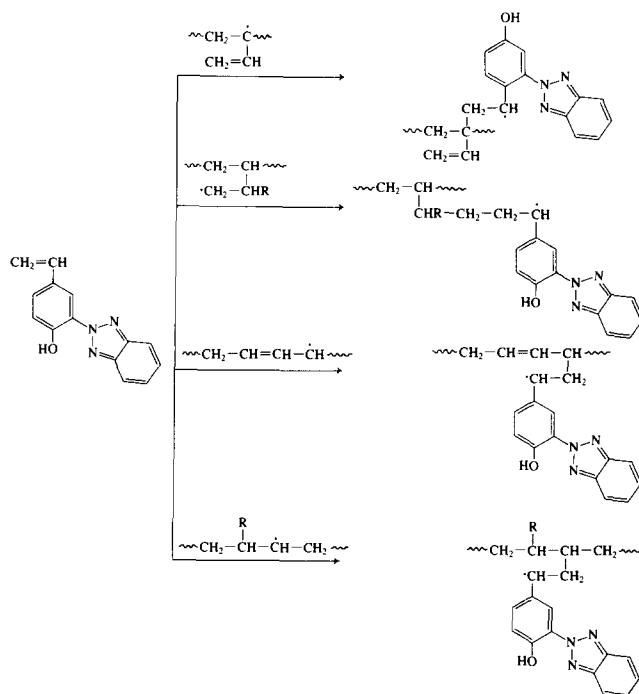*Preparation of vinyl-substituted 2(2-hydroxyphenyl)2H-benzotriazoles*

2(2-Hydroxy-5-vinylphenyl)2H-benzotriazole (2H5V)[35] was synthesized in six steps and in an overall yield of $\approx 40\%$ from 2-nitroaniline by two routes, each one representing one of the classical syntheses of styrene derivatives. In one case, the key intermediate had an ethyl group attached to the benzene ring and was obtained by condensation of 2-nitrobenzenediazonium chloride with 4-ethylphenol followed by reductive cyclization; the subsequent pathway to the vinyl group required bromination and dehydrobromination. The second route consisted of the condensation of *o*-nitrobenzene-diazonium chloride with 4-hydroxyacetophenone. The key intermediate of the second route, 2(2-hydroxy-5-acetylphenyl)2H-benzophenone, had an acetyl group attached to the benzene ring; the carbonyl group was reduced to the alcohol, which was then dehydrated. This was also the common intermediate for the synthesis of 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole (2H5P)[24]. The synthesis of 2(2-hydroxy-5-methylphenyl)2H-5-vinylbenzotriazole[36] was prepared by a sequence of reactions similar to those which gave 2H5V. The starting materials for this synthesis were, however, not 2-nitroaniline and 4-ethylphenol but 4-ethyl-2-nitroaniline and 4-methylphenol(*p*-cresol).

The vinyl monomer, 2H5V, but not the isopropenyl monomer 2H5P (low ceiling temperature), could be homopolymerized (equation (7)). When the copolymerization of 2H5V and 2H5P was carried out, copolymers were obtained which had copolymer compositions similar to those of the feed compositions. The copolymerization parameters of 2H5V and 2H5P with styrene, methyl methacrylate and *n*-butyl acrylate were determined in bulk using azobisisobutyronitrile as the initiator at 50°C (*Table 1*). The solubility of 2H5V and 2H5P in styrene, methyl methacrylate and *n*-butyl acrylate at 50°C limited the amount of the functional monomers that could be incorporated into the copolymer and for which the solubility parameters could be determined. The solubility of 2H5V is highest in styrene at 50°C at $\approx 20 \text{mol}\%$. In methyl methacrylate, 2H5V is soluble to $19 \text{mol}\%$ and in *n*-butyl acrylate the solubility of 2H5V is $14 \text{mol}\%$. 2H5P is less soluble: $11 \text{mol}\%$ in styrene, $10 \text{mol}\%$ in methyl methacrylate, and $11 \text{mol}\%$ in *n*-butyl acrylate.

As is usual for determination of the copolymerization parameter, the copolymerizations were stopped at conversions of 5-8%. The Kelen–Tudos equation was used for the calculation of the copolymerization parameters. Standard deviations of the copolymerization

parameter of 2H5V and 2H5P were higher than usual, because only low concentrations of the comonomer were in the copolymerization mixture. The copolymerization parameters are given in the table. The zero values of two copolymerization parameters of 2H5P with styrene or methyl methacrylate show that 2H5P is present in the polymer as isolated units. In the case of the copolymerization of 2H5P with *n*-butyl acrylate, the value of $r_2 = 0.76 \pm 0.25$ means that there exists some 2H5P-2H5P units in the copolymer. The low reactivity of *n*-butyl acrylate toward the propagating radical with 2H5P accounts for the fact that the values of the reactivity ratio, r_2, in the series: styrene, methyl methacrylate and *n*-butyl acrylate, were caused by the increased relative activity of 2H5V and 2H5P toward the propagating radical of the terminal vinyl monomer unit. On the other hand, the increased value of r_2 in the case of 2H5V is a result of a decreased vinyl monomer reactivity toward the terminal 2H5V propagating radical.

2H5V was grafted onto aliphatic C–H groups using ditertiary butyl peroxide as initiator and boiling chlorobenzene as the solvent[38]. Polymers onto which grafting was achieved were ethylene/vinyl acetate copolymer, an ethylene/propylene copolymer, atactic polypropylene, poly(methyl acrylate), and poly(methyl methacrylate). 2H5V was also grafted onto *cis*-1,4-polybutadiene and 1,2-poly-butadiene[37]. Solution grafting was easily accomplished with azobisisobutyronitrile as the initiator when low polymer concentrations were used(equation (8)).
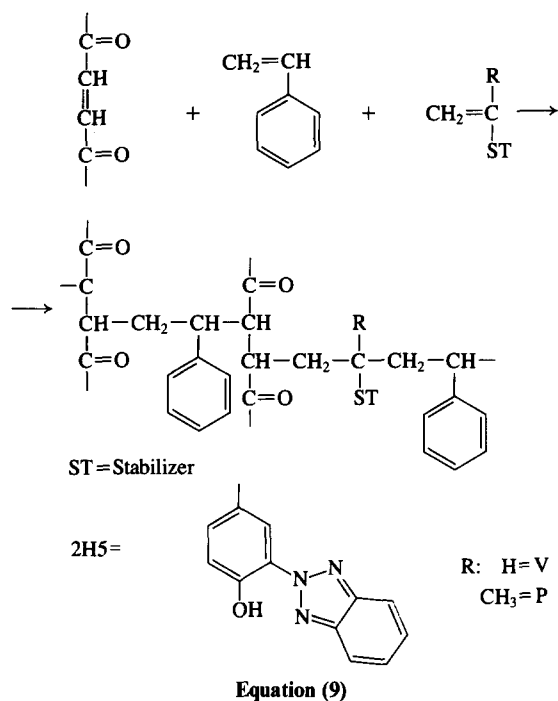

Equation (8)

2H5V and 2H5P have also been quantitatively incorporated into polymerizing mixtures of unsaturated polyesters and styrene with radical initiators[44] (equation (9)). Oligomeric polyesters prepared from maleic anhydride, phthalic anhydride and 1,3-propanediol (70 wt%) were dissolved in 30 wt% of styrene, 2H5V and 2H5P added in 0.5-5.0% amounts, and the mixture was polymerized. Selected compositions of these polymers were studied by e.s.c.a. spectroscopy. It is well known that e.s.c.a. spectroscopy can show the elemental composition

Table 1 Copolymerization parameters for vinyl monomers; styrene (St), methyl methacrylate (MMA), *n*-butyl acrylate (BuA) – M_1 with 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole (2H5V) and 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole (2H5P), respectively; M_2 at 50°C

M_1	M_2	r_1	r_2
St	2H5V	0.74±0.06	0.10±0.30
MMA	2H5V	0.45±0.01	1.18±0.30
BuA	2H5V	0.21±0.00	2.10±0.28
St	2H5P	1.07±0.08	0.0
MMA	2H5P	0.41±0.01	0.0
BuA	2H5P	0.12±0.00	0.76±0.26

ST = Stabilizer

R: H = V
CH₃ = P

Equation (9)

Equation (10)

Equation (11)

of compounds in 20 to 50 Å depth of the surface. In our case, the analysis was quite convenient because the nitrogen atoms of the triazole ring of the 2H5V and 2H5P units could be used to determine the composition of the u.v. stabilizers on the surface. Initially, the e.s.c.a. analysis showed that the amount of nitrogen (u.v. stabilizer) in the surface layer is similar to that analysed by elemental nitrogen analysis for the entire polymer. After accelerated ageing by vigorous photo-oxidation, where the polymer was excessively degraded on the surface, it was found that the nitrogen content of the surface layer had not decreased as one would expect if the stabilizer had been depleted from the surface. It actually increased substantially, indicating that the u.v. stabilizer had remained in place throughout the entire degradation procedure.

Simulated accelerated weathering tests of copolymers with 2H5V and 2H5P showed them to be effective stabilizers for acrylic polymers[45,46]. While the initial surface degradation of acrylic polymers (without stabilizers) in those accelerated tests started at the equivalence of a lifetime to failure of 6–8 years, the polymeric u.v. stabilizer-containing copolymers were stabilized to a lifetime to failure in excess of 20 years. More studies are needed to quantitatively determine the full utility of the polymeric stabilizers and to establish the optimum quantities required for their effective use.

Preparation of new 2(2-hydroxyphenyl)2H-benzo-triazoles

Reaction of 2-nitrobenzenediazonium salts with an excess of resorcinol (1,3-dihydroxybenzene) (equation (10)) or phloroglucinol (1,3,5-trihydroxybenzene) (equation (11)) gave (after reductive cyclization) not only monosubstituted benzotriazole derivatives but also di- and, in the case of phloroglucinol, even the tribenzotriazole-substituted compound. The u.v. spectrum showed that the disubstituted compounds have a very high extinction coefficient, more than twice that of monosubstituted 2(2-hydroxyphenyl)2H-benzotriazole,
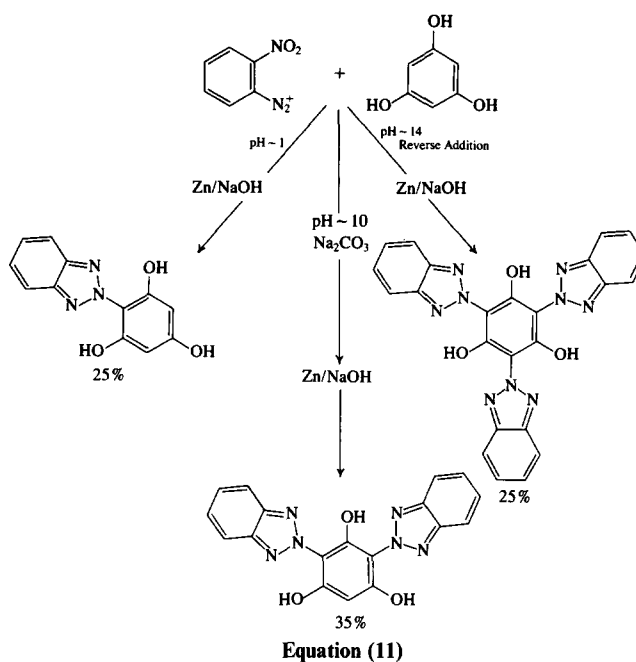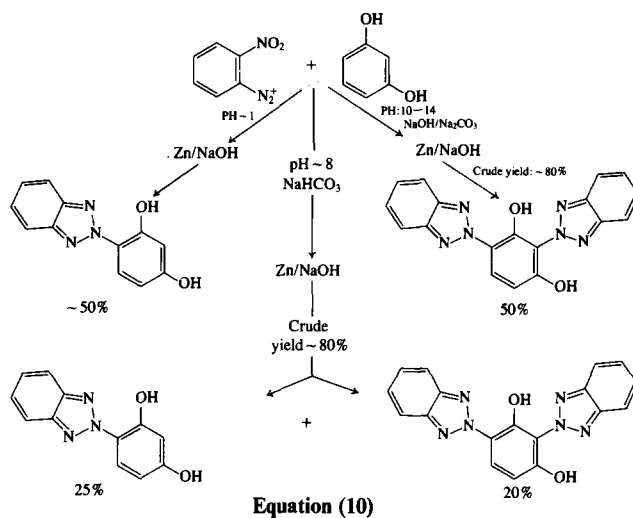
and an ultraviolet spectrum broadened to shorter wavelengths. The spectrum also retained the sharp drop of the extinction coefficient just at the border frequency of the visible spectrum. We expect these compounds to be exceptionally effective as u.v. stabilizers. Addition of a third benzotriazole ring does not significantly change the extinction coefficient which is increased by only ≈ 20%, but the u.v. absorption is substantially broadened to shorter wavelengths (*Figure 5*).

We have now worked out in detail the reaction conditions for the azo coupling reactions. By controlling the pH of the azo coupling, the reaction can be directed to either the mono- or disubstitution products in the case of resorcinol or to mono-, di- and trisubstitution in the case of phloroglucinol.

The monosubstitution product of resorcinol, 2(2,4-dihydroxyphenyl)2H-benzotriazole, is an excellent starting material for another family of polymerizable stabilizers. Reaction with acryloyl chloride or methacryloyl chloride gave 2[2-hydroxy-4-acryloxy(or methacryloxy)phenyl]2H-benzotriazole (equation (12), *Figure 6*).

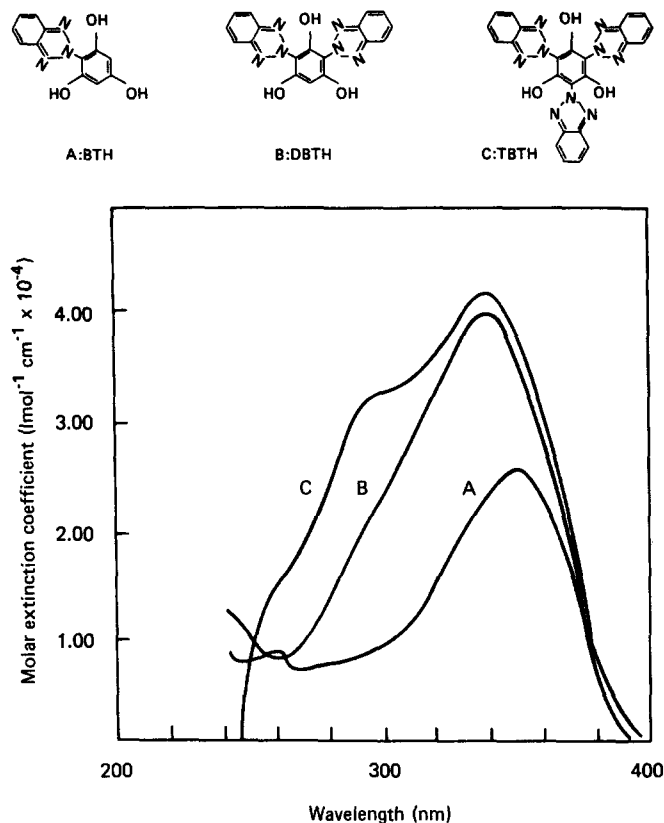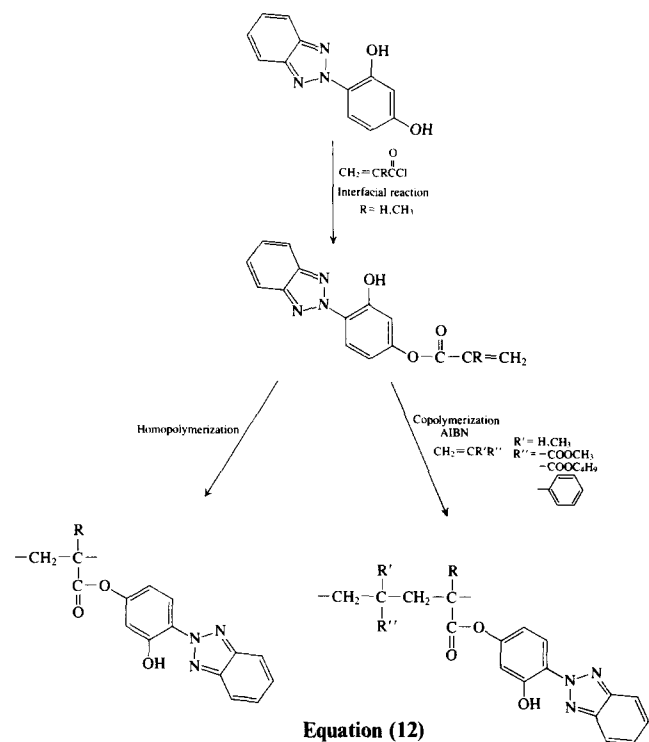The disubstitution product of resorcinol and the di- and

A:BTH   B:DBTH   C:TBTH

Figure 5 U.v. absorption showing substantial broadening to shorter wavelengths on benzotriazole ring addition to benzotriazole derivatives

Equation (12)

the tribenzotriazole substitution product of phloroglucinol could also be acylated to the 4-acryloxy(methacryloxy) derivatives which are again polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles with high extinction coefficients and desirable u.v. absorption.

We have synthesized u.v. absorbing compounds that have both benzophenone and benzotriazole units in the same molecule. These compounds were prepared from 2,4-dihydroxybenzophenone and 2-nitrobenzenediazonium chloride or 4-methoxy-2-nitrobenzenediazonium chloride. After reductive cyclization of the condensation product, only the disubstitution product could be obtained. The u.v. spectra of these compounds show broad absorptivity with four characteristic maxima, indicating a difference in the u.v. behaviour from the simple dibenzotriazole-substituted resorcinol and suggesting possibly unusual photophysical behaviour.

The vinyl and isopropenyl derivatives of 2(2,4-dihydroxyphenyl)1,3-2H-dibenzotriazole were also synthesized from dibenzotriazole-substituted 2,4-hydroxyacetophenone. The compound, 2(2,4-dihydroxy-5-acetylphenyl)1,3-2H-dibenzotriazole, was reduced to the secondary alcohol with zinc borohydride. The alcohol was then dehydrated to 2(2,4-dihydroxy-5-vinylphenyl)1,3-2H-dibenzotriazole. When reacted with methylmagnesium iodide, 2(2,4-dihydroxy-5-acetylphenylene)1,3-2H-dibenzotriazole gave the tertiary carbinol which was readily dehydrated to 2(2,4-dihydroxy-5-isopropenylphenyl)1,3-2H-dibenzotriazole.

4-Methoxy-2-nitroaniline was a convenient starting material for two additional aspects of our synthetic work on 2(2-hydroxyphenyl)2H-benzotriazoles. The methoxy group influenced the absorption spectra of the u.v. absorbers (stabilizers) by extending the maximum of the u.v. absorption by $\approx 15\,nm$ to higher wavelengths, from $\approx 340\,nm$ for the unsubstituted 2(2-hydroxyphenyl)2H-benzotriazoles to $355\,nm$ for the 4-methoxy-substituted 2(2-hydroxyphenyl)2H-benzotriazoles (equation (13)). The methoxy group could readily and quantitatively be cleaved with hydrogen bromide in dimethylformamide to the hydroxy compound as shown for 2(2,4-dihydroxyphenyl)1,3-2H-*bis*-(4-methoxy benzotriazole) (equation (14)). 2(2,4-Dihydroxyphenyl)2H-4-methoxy-benzotriazole is a useful intermediate for the preparation of the 4-acryloxy or 4-methacryloxy compounds which are useful as acrylic monomers for polymerization and copolymerization. It can also be demethylated to 2(2,4-dihydroxyphenyl)2H-4-hydroxybenzotriazole, which has an excellent potential as a polymer-bound stabilizer for polyesters, polycarbonates, polyurethane and epoxy resins. Reaction of 2 mols of 4-methoxy-2-nitrobenzenediazonium chloride
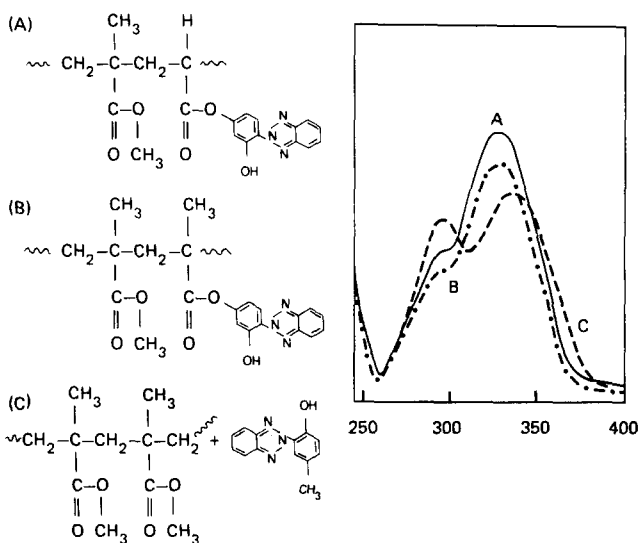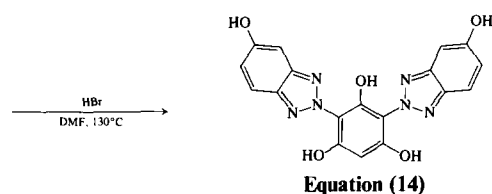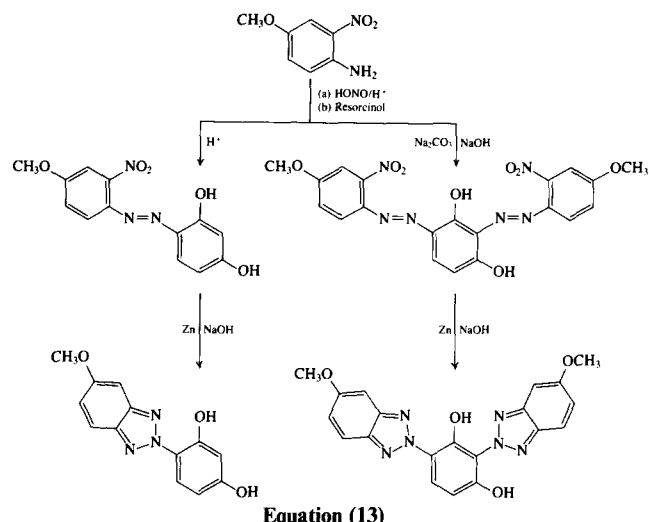

Figure 6 U.v. absorption of 2[2-hydroxy-4-acryloxy(and methacryloxy)phenyl]2H-benzotriazole (see Equation (12))

Equation (13)

Equation (14)

with resorcinol or phloroglucinol and reductive cyclization gave 2(2,4-dihydroxyphenyl)1,3-2H-di(4-methoxybenzotriazole) and 2(2,4,6-trihydroxyphenyl)1,3-2H-di(4-methoxy-benzotriazole). These two compounds could be demethylated to 2(2,4-dihydroxyphenyl)1,3-2H-di(4-hydroxybenzotriazole) and 2(2,4,6-trihydroxyphenyl)1,3-2H-di(4-hydroxybenzotriazole), respectively, and are of potential interest for incorporation into epoxy resins by virtue of their two 4-hydroxy groups in the benzotriazole rings. (The *ortho* hydroxy groups are hydrogen bonded to the triazole ring and are known to be much less reactive. In fact, radical polymerization can be carried out in the presence of compounds with hydrogen-bonded *ortho* hydroxy groups without the *ortho* hydroxy groups interfering in radical polymerization[21].)

In conclusion, several new classes of 2(2-hydroxyphenyl)2H-benzotriazole u.v. stabilizers have been prepared. 2(2-Hydroxyphenyl)2H-benzotriazoles with two benzotriazoles in the molecule or with benzotriazole and benzophenone groups have given new u.v.-absorbing systems, and 2(2-hydroxyphenyl)2H-benzotriazoles substituted with hydroxy groups in the benzotriazole rings have made 2(2-hydroxyphenyl)2H-benzotriazole u.v. stabilizers available for incorporation into numerous types of polymers.

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