Synthesis and Polymerization of UV Stabilizing Monomers: Synthesis and Polymerization of 2-Hydroxy-4-(2-methacryloylethoxy)benzophenone and 2-(2H-Benzotriazol-2-yl)-4-methyl-6-vinyl Phenol

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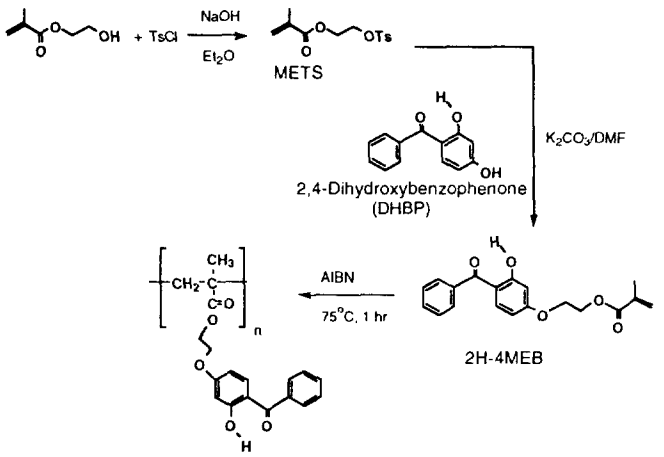
Received June 14, 1993

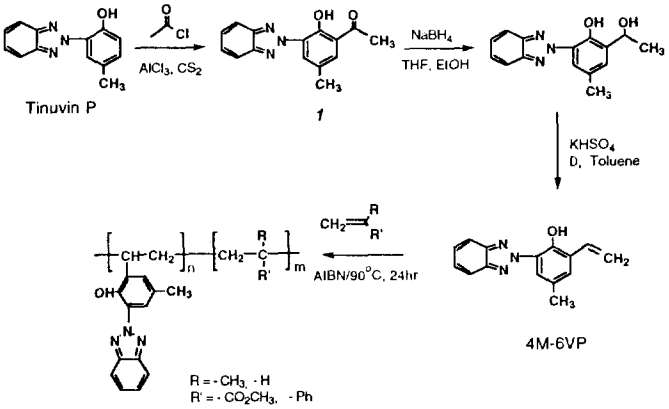
The stabilization of organic polymeric materials toward the ultraviolet light (UV) is generally achieved by simply adding the proper UV stabilizers to the materials. Two of the most widely employed UV stabilizers series in today's polymer industry are the derivatives of 2-hydroxybenzophenone (BP) and 2-hydroxyphenylbenzotriazole (BT).[1] But the range of application of theses two series of UV stabilizers is often severely restricted due to the limited compatibility of these additives with the polyolefins such as polyethylene (PE), polystyrene (PS) and polymethylmethacrylate (PMMA). Because of the limited compatibility of BP's and BT's, these additives may be leached out of the polymer matrix during the polymer processing, especially at the elevated temperature, as well as after prolonged use of the material. The problem has been circumvented by introduction of the nonpolar bulky groups such as alkyl groups on to the phenyl ring of the UV stabilizer molecule or by use of the oligomeric (polymeric) UV stabilizers.[2] But if UV stabilizers having the polymerizable substituents already on the molecule were readily available and these functional monomers were copolymerized with the bulk monomers, the problem of '*leaching out*' would be disappeared and the lifetime of the material be prolonged. Thus we have initiated the study on the synthesis and polymerization of UV stabilizing functional monomers.

Our general strategy for the synthesis of UV stabilizing functional monomers was not to design a new synthetic route to the UV stabilizer itself, but just to introduce the polymerizable groups to the existing BP and BT. Having two -OH groups on the phenyl ring, one at the *ortho-* and the other at the 4- position to the carbonyl group, 2,4-dihydroxybenzophenone (DHBP) was first chosen as a candidate for the synthesis of the polymerizable UV stabilizer. It was anticipated that the reactivity difference of the two -OH groups on the DHBP molecule was sufficient enough to ensure the introduction of the polymerizable group only to the 4-position, since the -OH group at the *ortho-* position was hydrogen bonded to the carbonyl oxygen.[3] Thus 20 mmoles of DHBP was reacted with 15 mmoles of 2-methacryloyloxyethyl-*p*-toluene sulfonate (METS) in diemthylformamide in the presence of potassium carbonate at 110℃ to obtain a UV stabilizing functional monomer, 2-hydroxy-4-(2-methacryloylethoxy)benzophenone (2H-4MEB) in 34% yield.[4] The METS, which could easily and safely be handled and stored, unlike methacryloyl chloride, was prepared from 2-hydroxyethyl methacrylate (HEMA) and *p*-toluene sulfonate in 97% yield (Scheme 1).[5]

The spectral data (NMR, UV and IR) of 2H-4MEB showed



Scheme 1.



Scheme 2.

that the -OH group in the DHBP at the *ortho-* position was not reacted under this reaction condition. Homopolymerization of 2H-4MEB and co-polymerization of 2H-4MEB with 99, 97 and 90 mole% each of HEMA and MMA using 0.3 mole% of AIBN as an initiator afforded the corresponding polymers in 30-75% yields. UV spectra of the polymers prepared clearly showed the presence of the chromophore of 2H-4MEB. The molecular weight ($\bar{M}_n$) measured by GPC of the homopolymer of 2H-4MEB was 5,500, which seemed a little low for the methacrylate polymers, while those of copolymers with MMA ranged from 6,400 to 46,000 depending on the 2H-4MEB content. It was interesting to note that $\bar{M}_n$ increased as the mole fraction of 2H-4MEB increased from 1% to 10% of MMA.

Having finished the synthesis of one of the BP series functional monomers, we have turned our effort to the synthesis of polymerizable BT series UV stabilizers, which is shown in Scheme II. Friedel-Crafts acylation of 18 mmoles of 2-(2H-Benzotrazol-2-yl)-4-methyl phenol (Tinuvin P™) with 80 mmoles of acetyl chloride and 120 mmoles of $AlCl_3$ in CS_2 solvent transformed the Tinuvin P into its acetyl derivative **1** in 72% yield. The hydroxyl group on the phenyl ring of Tinuvin P was intact after the reaction as evidenced by UV and IR spectra. This was much improved method for the synthesis of the intermediate **1**, which had been prepared previously by a sequence of four reactions starting from nitroaniline in 27% yield.[6] To transform the newly introduced

acetyl group into the polymerizable vinyl group, the compound **1** was reduced with $NaBH_4$ and the resulting alcohol was dehydrated by $KHSO_4$ to obtain the desired UV stabilizing functional monomer, 2-(2H-benzotriazol-2-yl)-4-methyl-6-vinyl phenol (4M-6VP) in 70% yield (Scheme 2).[7]

Attempt of homopolymerization of 4M-6VP using 0.5 mole% of AIBN as an initiator was unsuccessful. The starting 4M-6VP was recovered even after 24 hr of polymerization at 90℃. But copolymerization of 4M-6VP with 99 mole% of MMA and styrene proceeded smoothly to produce the corresponding copolymers in 40 and 59% yields. There is a report that the polymerization of 2-(2H-benzotriazol-2-yl)-4-vinyl phenol, which had vinyl group at the 4-position of the phenyl ring of the BT molecule, proceeded smoothly.[8] However, this is the first report on the polymerizable BT's in which polymerizable group is attached at the 6- position of the phenyl ring of BT.

Acknowledgement. This work was supported in part by the Korea Research Foundation through Non Directed Research Fund, 1990.

References

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4. Spectral data for 2H-4MEB (mp. 82-84℃): ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 3H), 4.4 (m, 4H), 6.2 (s, 1H), 6.4 (m, 3H), 7.7 (m, 6H), 12.6 (s, 1H); IR (KBr) 3500, 1680, 1620 cm^{-1}.
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7. Spectral data for 4M-6VP (mp. 110-112℃): ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 3H), 5.6 (dd, 2H), 6.8-8.0 (m, 7H), 11.6 (s, 1H); IR (KBr) 3300, 1420 cm^{-1}.
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Inhibition and Active-Site Requirements of 5-Aminolevulinic Acid Dehydratase

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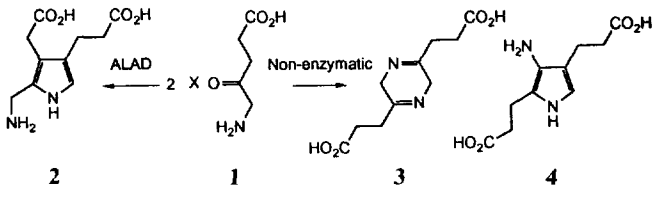
Received June 18, 1993

5-Aminolevulinic acid dehydratase[1] (ALAD, porphobilinogen synthase EC 4.2.1.24), found in both plants and animals, catalyzes the transformation of two 5-aminolevulinic acid (ALA, **1**) molecules into porphobilinogen (PBG, **2**), one pyrrole unit of the tetrapyrrolic pigments such as chlorophylls, hemes, phycobilins, and cobalamins.[2]



Scheme 1.

This enzyme requires an exogeneous thiol such as mercaptoethanol, dithioerythritol or dithiothreitol and metal ion Zn^{2+}, for the full catalytic activity.[1,3] Though the molecular weights[4] and amino acid sequences[5] of this enzyme from several sources were known, no X-ray picture of this enzyme has yet been revealed. Furthermore, no systematic study to find out the structural requirements for binding to ALAD has been undertaken.[6] The importance of proper binding of two substrates at the active site of ALAD is realized by comparison of enzymatic and non-enzymatic reaction of ALA (Scheme 1). PBG has never been formed by a chemical method from ALA.[7] Instead two moles of ALA are condensed in acid and/or base to yield 2,5-(β-carboxyethyl)dihydropyrazine (**3**) as the major product with a relatively small amount of pseudo-PBG (**4**). The structural requirements of ALAD enzyme can be assessed by inhibition studies of some simple substrate analogues (**5-9**).

Compounds **5-7** were designed to find out the relative importance of the three functional groups attached to the natural substrate, amine, ketone and carboxylate. Compounds **8** and **9** can give an insight into the electronic environment required for proper binding. We report herein the results of the inhibition of the enzyme isolated from bovine liver[8] by simple substrate analogues.

Compounds **5, 7** and **8** were purchased from Aldrich and purified prior to use. 1-Amino-2-pentanone (**6**) was prepared by bromination[9] and amination[10] of 2-pentanone. 5-Fluorolevulinic acid (**9**) was obtained by the reported method.[11]

ALAD was assayed by a modified literature procedure.[12] The enzyme ALAD from bovine liver, purchased from SIGMA (1.5 unit/mg protein), was diluted with 0.10 M sodium phosphate buffer containing 0.1 mM $ZnSO_4$ and 20 mM of dithiothreitol, pH 6.8. This enzyme solution (0.2-0.3 unit/ as stable enough to keep in refrigerator for a few weeks. The standard enzyme assay contained 0.15 m*l* of 0.10 M sodium phosphate buffer containing 0.1 mM $ZnSO_4$ and 20 mM of dithiothreitol, pH 6.8, 0.15 m*l* of a solution of crystalline 5-aminolevulinate hydrochloride in distilled water, 0.10 m*l* of buffer or inhibitor solution, and 0.10 m*l* of enzyme solution. The blank was prepared by using boiled enzyme solution instead of the active one. After incubation for 30 min at 37℃, the reaction was terminated by addition of 0.5 m*l* of 0.1 M $HgCl_2$ in 10% trichloroacetic acid and added 0.5 m*l* of modified Ehrlich's reagent, which was prepared by dissolving 4-dimethyl aminobenzaldehyde (2 g) in a mixture of 80 m*l* glacial acetic acid and 20 m*l* 60-62% perchloric acid. After 15 min at room temperature the resultant precipi-