

Review

SYNTHESIS AND CHARACTERIZATION OF NEW STABILIZERS WITH OPTIMAL MOLECULAR WEIGHT*

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Abstract Over 2×10^8 tons of polymers are produced every year, and a large portion of polymers faces the degradation problem. There are many effective methods to protect polymers against degradation and the addition of stabilizers to polymer remains the most convenient and effective way of enhancing polymer life and performance. In this article, a series of effective stabilizers with optimal molecular weight (MW), including common, monomeric and polymeric stabilizers (antioxidant and light stabilizer) were synthesized using isocyanation, controlled isocyanation, hydrosilylation, epoxide addition, macro-reaction of stabilizing functional compounds and polymerization of monomeric stabilizers. The structure and performance of these new stabilizers were characterized by using IR, NMR, MS, UV-spectra, XPS and elemental analysis. The current development of stabilizer synthesis was also reviewed.

Keywords Preparation of stabilizer, Antioxidant, Hindered amine light stabilizer, Isocyanation, Hydrosilylation

INTRODUCTION

Polymer materials exposed to sunlight, used at elevated temperatures, or stored at room temperature in air undergo degradation which shortens their service life. The first effect is associated with photo-oxidation, and the second is mainly a consequence of thermal oxidation. There are several ways to prevent thermal oxidation and photo-oxidation of polymers and the addition of stabilizers (antioxidants and light stabilizers) is the most convenient and effective way as stabilizer addition will not alter processing conditions to any significant extent and there are many effective stabilizers to choose^[1-11].

Based on the literature and our results, one can understand that the stabilizing effectiveness of stabilizers are closely related to their thermal stability, their compatibility and their mobility in the substrate. The structure and molecular weight of stabilizers are also very important^[3-8, 11, 12]. Current trends are to synthesize stabilizers with optimal MW, with multifunctional properties, and with macromolecularization so as to enhance their effectiveness and to synthesize stabilizers which are more eco-friendly^[3-6].

In this article, we report our work on the synthesis of new antioxidants and light stabilizers with optimal M_w by the new routes. The characterization of structure and performance for these new stabilizers are also described.

Synthesis and Characterization of Common Stabilizers

Synthesis of light stabilizers

The destruction of polymer materials exposed to sunlight in air is mainly associated with the photo-oxidation of polymers. Addition of effective light stabilizers to substrate is the most convenient and effective way to prevent polymer photo-oxidation. There are four generations of stabilizers to protect polymers against photo-oxidation, namely screeners such as carbon black, Cr_2O_3 , Fe_2O_3 , quenchers such as nickel chelate, UV-absorbers such as *o*-

* The work cited in this review was supported by the National Natural Science Foundation of China (No. 928700801 and No 2880201), the Polymer Physics Laboratory, Academia Sinica and National University of Singapore Grant RP 3960694.

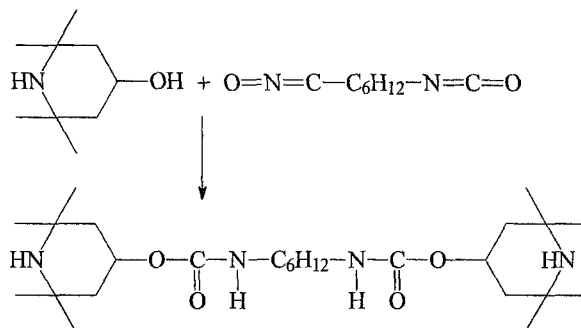
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Received September 4, 2000; Revised October 22; Accepted October 24, 2000

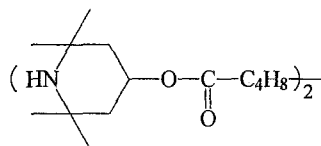
hydroxy benzophenone, *o*-hydroxy benzotriazol and free radical scavengers^[1-4]. The hindered amine light stabilizers (HALS) belonging to the free radical scavengers are the most effective light stabilizers. Study results show that there is an optimal MW for stabilizers, too high MW and too low MW make the stabilizer effectiveness poor, the former is associated with poor mobility of stabilizer in substrate and the latter is related to their poor thermal stability^[3-8, 11, 12]. The newest results show that the optimal MW for light stabilizers is in a range of 400–600^[3-8, 11, 12].

There are many methods to synthesize stabilizers and isocyanation is a very useful one. Our studies show this synthetic reaction to be stoichiometric and exothermic, it is a fast reaction with moderate reaction conditions and high yield and the end product stabilizer is easy to purify^[13-15].

Highly effective light stabilizers with optimal molecular weight can easily be prepared by the direct isocyanation of photo-stabilizing functional compounds (hindered piperidine derivatives, UV-absorber) with isocyanates^[13-15]. 12 highly effective hindered amine light stabilizers (HALS) with optimal MW have been prepared by the direct isocyanation of hindered piperidine derivatives [2,2,6,6-tetramethyl-4-piperidinol (TMP), 1,2,2,6,6-pentamethyl-4-piperidinol (PMP), 4-amino-2,2,6,6-tetramethyl-piperidine (ATMP)] with isocyanates [octadecyl isocyanate (OI), hexamethylene diisocyanate (HMDI), toluene 2,4-diisocyanate (TDI), methylene diisocyanate (MDI)]^[14].



Their structures have been confirmed by IR, NMR, and elemental analysis. The photo stabilizing effectiveness of these new HALS is shown in Fig. 1. From Fig. 1, it can be seen that the effectiveness of these new HALS for protecting polypropylene against photo-oxidation is comparable to that of Tinuvin-770 which is a very effective commercial light stabilizer^[14].



Tinuvin 770

Four new UV-absorbers with optimal MW have been synthesized by direct isocyanation of 2,4-dihydroxybenzophenone (DHBP) with diisocyanate (OI, HMDI, TDI, MDI), their structures have been characterized by IR, NMR, MS, UV-spectroscopy and elemental analysis^[14].

Synthesis and characterization of new antioxidants

Aromatic amine and hindered phenol are two kinds of effective antioxidants which have been widely used. Hindered phenol antioxidant formed from 2,6-di-*tert*-butylphenol is the most effective antioxidant^[16, 17]. Recent studies show that hindered phenol antioxidant will displace the aromatic amine antioxidants owing to the toxicity and color staining problems of aromatic amines^[16, 17]. Optimal MW for antioxidants is in the range of 500–1000. Such antioxidants are considered for use at higher thermal processing temperature and against thermal oxidation at higher temperature^[3-6, 16, 17].

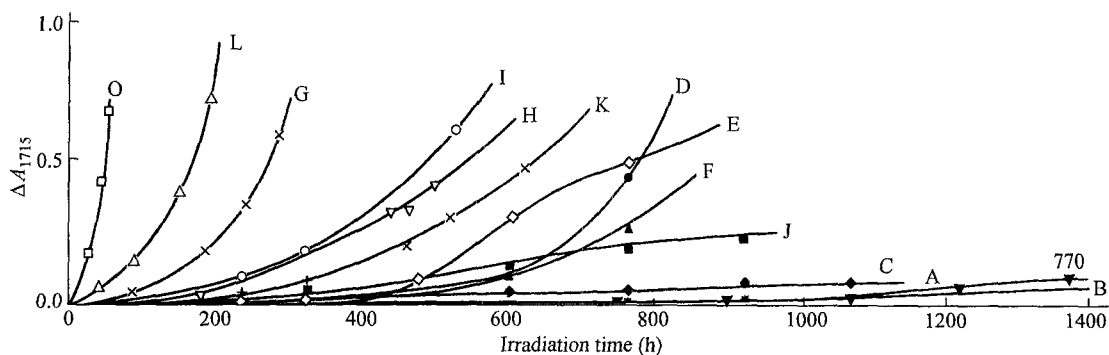


Fig. 1 Photo-stabilizing effectiveness of new HALS for PP film containing 0.3 wt% of HALS

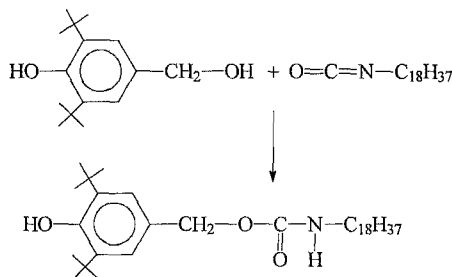
O: blank(PP-film)

Samples A-L are PP film samples each containing 0.3 wt% of new HALS A to L.

Sample 770 is a PP film sample containing 0.3 wt % of Tinuvin-770.

HALS A-L were produced from reaction of OI + TMP(A), HMDI + TMP(B), TDI + TMP(C), MDI + TMP(D); OI + PMP(E), HMDI + PMP(F), TDI + PMP(G), MDI + PMP(H); OI + ATMP(I), HMDI + ATMP(J), TDI + ATMP(K), MDI + ATMP(L).

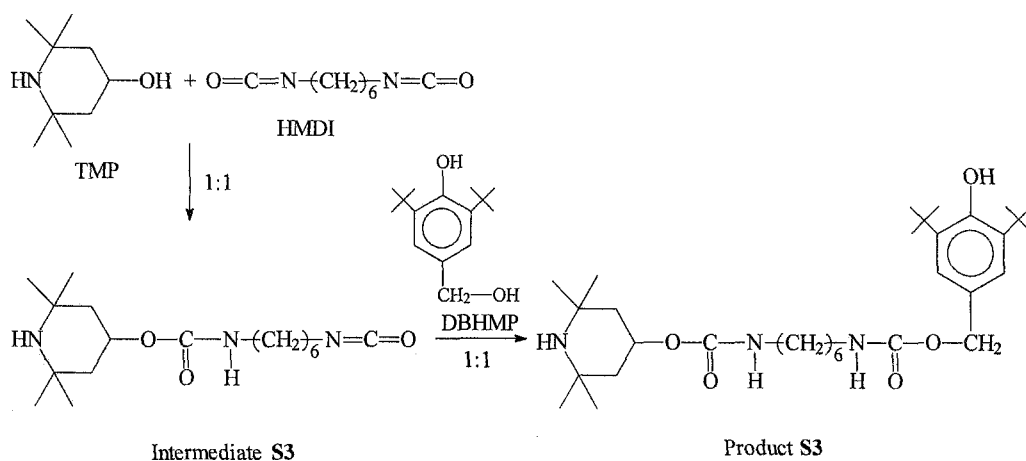
Effective antioxidants of higher molecular weight can be synthesized by direct isocyanation of 2,6-di-tert-butyl-4-hydroxy methyl phenol (DBHMP) with isocyanates^[18]:



Five new hindered phenol antioxidants with optimal MW have been prepared by direct isocyanation of 3,5-di-tert-butyl-4-hydroxy methyl phenol (DBHMP) with isocyanates (OI, TDI, MDI, HMDI and isophorone diisocyanate, IPDI). Their structures have been characterized by IR, NMR and elemental analysis. Results show that the increase in the MW of the antioxidant by isocyanation enhances its thermal stability. Hence, as shown in Fig. 2, its stabilizing effectiveness for protecting PP against thermal oxidation is enhanced. Introduction of very long alkyl chains into the antioxidant can effectively improve the compatibility of the antioxidant in the polymer substrate, hence increasing the effectiveness of the antioxidant^[18].

Synthesis of multifunctional stabilizers

The synthesis of stabilizers with multifunctional stabilizing action is one of the trends for developing new effective stabilizers. Six bifunctional stabilizers with optimal MW have been synthesized by a two-step controlled isocyanation of functional compounds containing active proton, such as $-\text{OH}$ in DHPB (2,4-dihydroxyl benzophenone), DBHMP or TMP (2,2,6,6-tetramethyl-4-piperidinol) with diisocyanates (TDI, HMDI)^[19]:



Their structure was determined by IR, NMR and elemental analysis. Results show that these bifunctional stabilizers are effective stabilizers for protecting polypropylene against both thermal oxidation and photo-oxidation^[19].

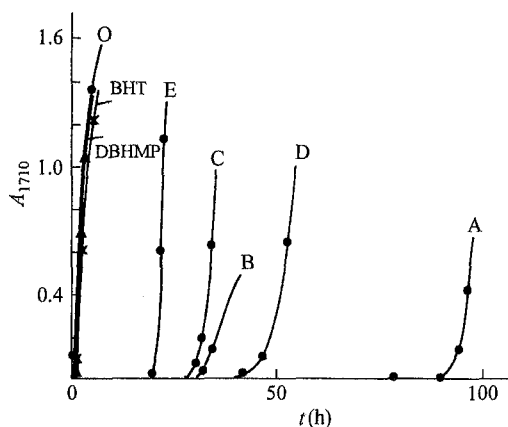
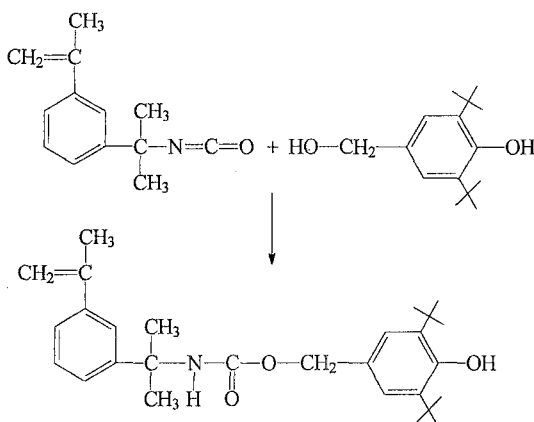


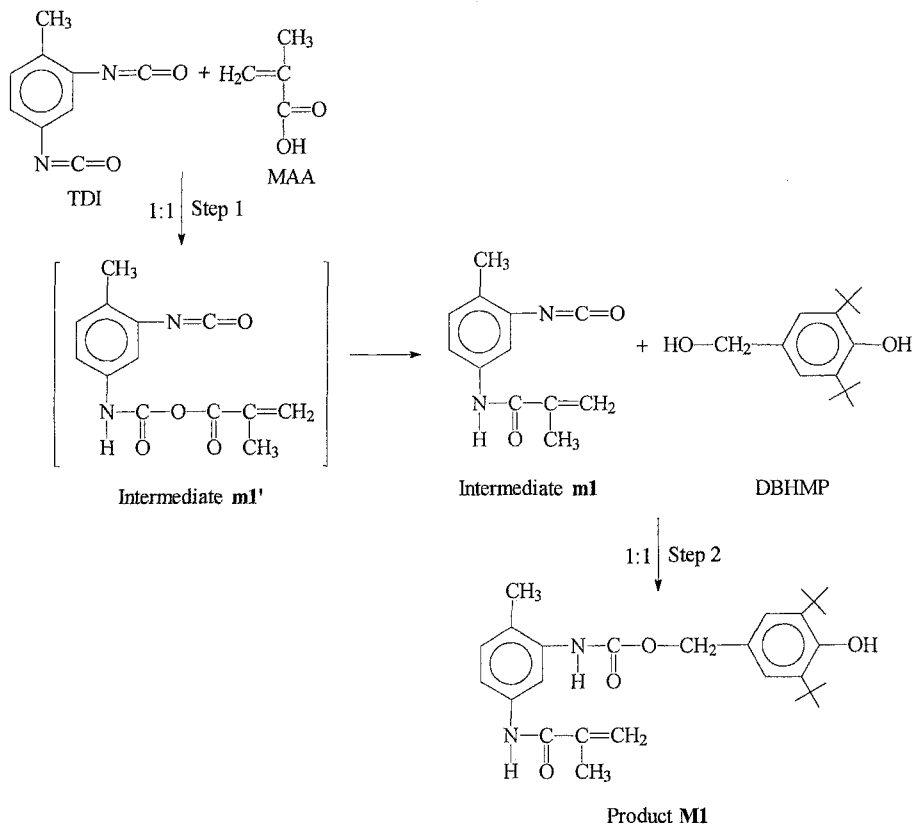
Fig. 2 Stabilizing effectiveness of new antioxidants for protecting PP-film against thermal oxidation at 140°C in air
 O-blank (PP-film), samples A-E are PP-film samples each containing 0.1% of the new antioxidant A, B, C, D and E, respectively; sample BHT is a PP-film containing 0.1% of commercial antioxidant 2,6-di-tert-butyl-4-methyl phenol (BHT) and sample DBHMP is a PP-film containing 0.1% of DBHMP. New antioxidants A to E were prepared from direct isocyanation of DBHMP with OI(A), TDI(B), HMDI(C), IPDI(D) and MDI(E).

Synthesis and Characterization of Monomeric Stabilizers

Functional polymers have attracted great attention. Synthesis of functional monomers, of course, is the first step for making functional polymers. Many reports pointed out that direct isocyanation of unsaturated monomers containing isocyanate with functional compounds containing active proton is a very useful route for preparing functional monomers^[3-6, 20-25].

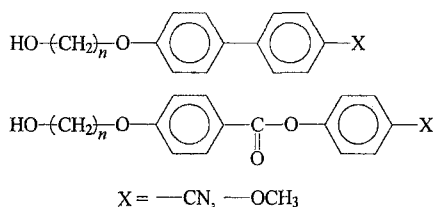


Six monomeric HALS have been synthesized by direct isocyanation of TMP, PMP and ATMP with unsaturated isocyanates, *m*-isopropylene- α,α -dimethylbenzyl isocyanate (*m*-TMI) and allyl isocyanate (AI)^[3-6, 12, 20, 21]. Their structures have been confirmed by IR, NMR, MS, XPS and elemental analysis. Two new monomers containing UV-absorber have been prepared by direct isocyanation of DHBP with unsaturated isocyanates (*m*-TMI, AI)^[22]. Two new monomeric HALS have been synthesized by epoxide addition reaction of ATMP to unsaturated epoxide^[23]. Five new monomeric antioxidants have been synthesized by direct isocyanation of DBHMP with isocyanates (*m*-TMI and AI) and by controlled isocyanation in two steps^[24]. In the first step an α,α -unsaturated acid, such as methacrylic acid (MAA) or acrylic acid (AA), reacts with diisocyanate (TDI, HMDI) at a 1 to 1 mole ratio, whereby one of the two isocyanate groups ($-\text{N}=\text{C}=\text{O}$) is converted to carry a double bond ($-\text{C}=\text{C}-$). This newly formed compound can be used as an intermediate which through further isocyanation with functional compounds containing active proton yields new functional monomers:

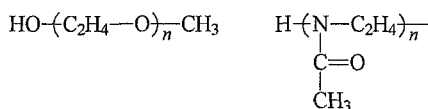


According to the above two-step controlled isocyanation, we have also synthesized six new monomeric light stabilizers^[25].

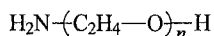
It should be pointed out that both the direct isocyanation of unsaturated isocyanate monomer and the controlled isocyanation of diisocyanate with unsaturated acids offer an effective method for preparing functional monomer when functional compounds containing active proton are used. For example, we can use the following functional compounds containing active proton to prepare functional monomers by isocyanation of unsaturated isocyanates and hence to make side chains for liquid crystalline polymers:



For polymeric surfactants, such as:



For modifying the wetting property of polymers:

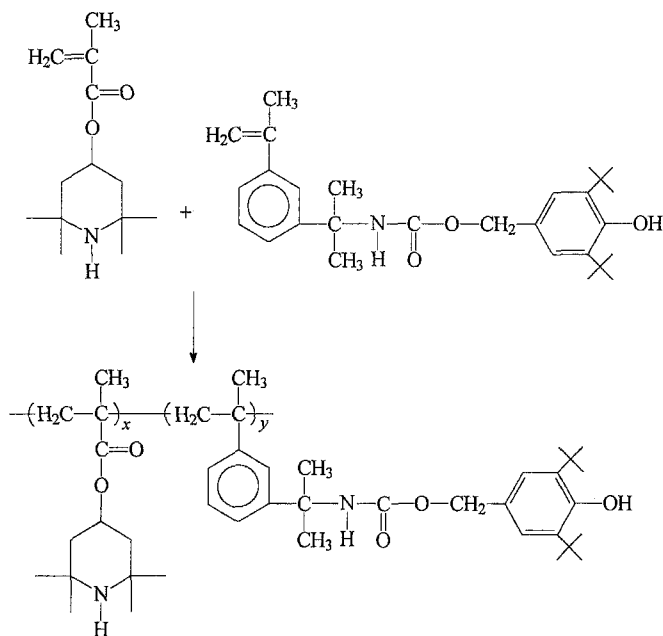


Functional monomers can also be used for making functional polymers.

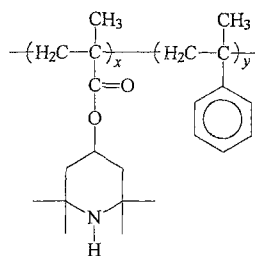
Synthesis of Polymeric Stabilizers

Investigation results show that stabilizers with low MW are relatively volatile and are easily extracted by liquids. A new trend for stabilizer development is to prepare stabilizers with higher MW or polymeric stabilizers. Optimal MW for polymeric stabilizer is in a range of 1000–3000 which is considered to provide a balance among thermal stability, mobility and extraction resistance and effectiveness^[3-8, 10, 11].

Polymeric stabilizers can be produced through co-polymerization, macromolecular functional reaction and the hydrosilylation of monomeric stabilizers:



Five polymeric HALS have been synthesized by co-polymerization of 2,2,6,6-tetramethylpiperidiny methacrylate (MTMP) with styrene, acrylonitrile, acrylamide, vinyl acetate and vinylpyridine^[26]. The stabilizing effectiveness for some of these new polymeric HALS are higher than that for the PDS, which is a useful industrial polymeric HALS produced in China^[26].

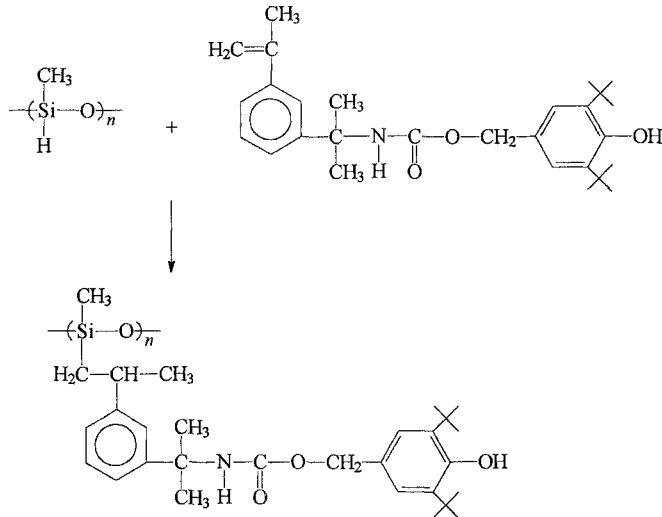


PDS

Eight polymeric stabilizers have been synthesized from the mixture copolymerization of ATMP, unsaturated epoxide and vinyl monomers (styrene and methyl methacrylate)^[27]. These polymeric light stabilizers are very resistant to liquid extraction and they possess higher thermal stability; their effectiveness for protecting polypropylene against photo-oxidation is much higher than that of the PDS produced in China^[27].

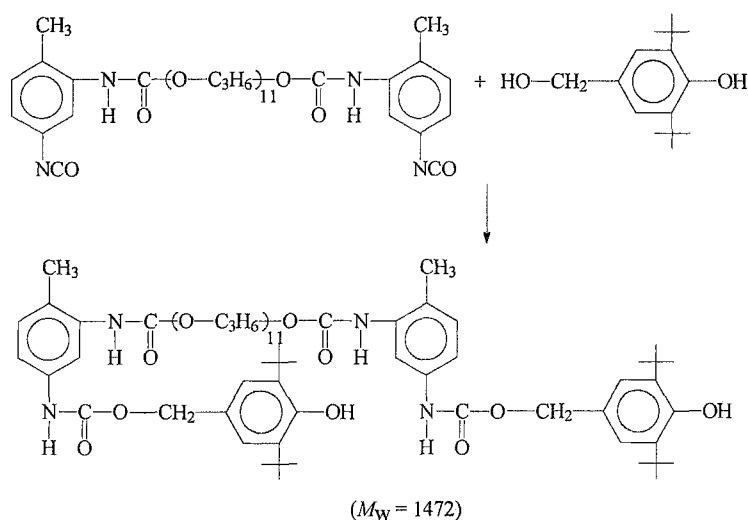
Polymeric stabilizers have been synthesized by co-polymerization of new monomeric hindered amines (HA) containing a urethane structure with vinyl monomers (styrene and methyl methacrylate)^[28]. A polymeric stabilizer containing both HA and UV-absorber function has been synthesized by co-polymerization of monomeric HA and monomeric UV-absorber^[29].

Polymeric stabilizers can also be prepared by hydrosilylation of monomeric stabilizers^[5, 30, 31].

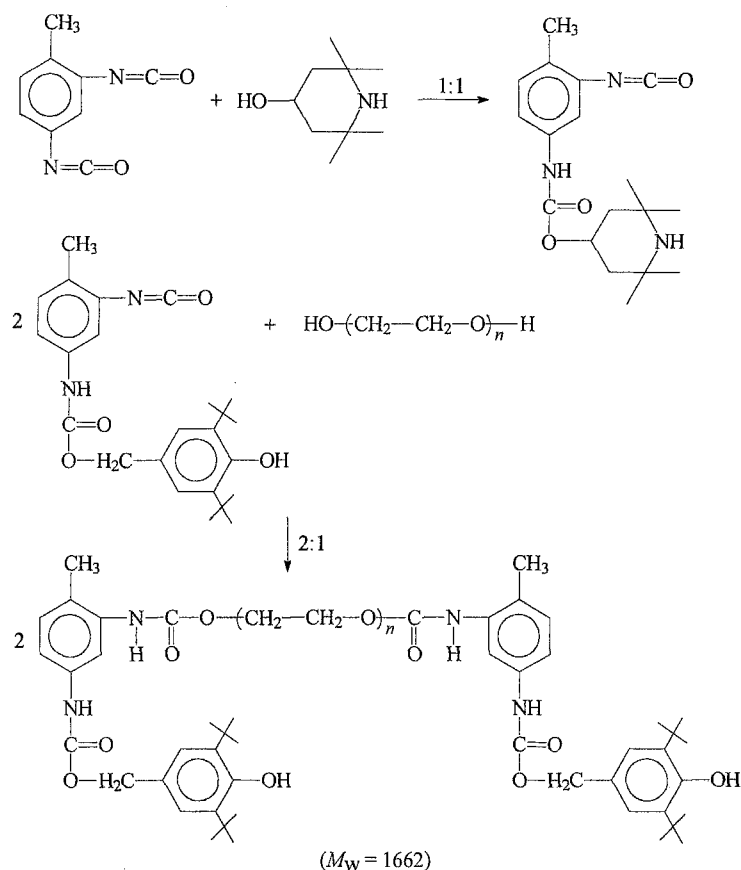


Polymeric stabilizers can also be prepared by macromolecular reaction^[3-6, 31].

Two new polymeric HALS and one polymeric antioxidant with optimal MW were synthesized by a macromolecular functional reaction of poly(propylene glycol) terminated with TDI ($M_w = 1000$) with TMP, ATMP and DBHBP^[3-6, 31].



Two new polymeric HALS and one polymeric antioxidant with optimal MW have also been synthesized through a controlled isocyanation and a macromolecular functional reaction, in which TDI with TMP, ATMP, DBHMP and poly(ethylene glycol) ($M_w = 1000$) were used^[31]:



It should be pointed out that the MW of these polymeric stabilizers can be accurately controlled by using the macromolecular functional reaction or the controlled isocyanation-macromolecular functional reaction shown

above, because the raw materials (original reactants) used in the above two routes are accurately known.

New polymeric HALS from copolymer of propylene and 2,2,6,6-tetramethyl-4-piperidiny1 maleate has been synthesized by a two-step approach, in which, the first step is to prepare copolymer of propylene with maleic anhydride by free radical polymerization (AIBN as the initiator), the second step is to prepare polymeric HALS by the reaction of TMP with the above copolymer in the presence of a catalyst, $\text{Ti}(-\text{OBut})_4$ ^[32].

CONCLUSIONS

Based on the above brief review of our work on the synthesis of stabilizers, we can conclude: (1) Isocyanation of stabilizing functional compounds containing active proton is a very useful reaction for synthesizing new stabilizers. Effective light stabilizers (HALS and UV-absorber) and antioxidants (hindered phenol) with optimal MW have been prepared by direct isocyanation of isocyanate (OI) or diisocyanates (TDI, HMDI, MDI) with piperidine derivatives (TMP, PMP, ATMP), 2,4-dihydroxybenzophenone (DHBP) and 2,6-di-tert-butyl-4-hydroxymethylphenol (DTHMP). Bisfunctional stabilizers containing antioxidant-HA, HA-UV-absorber and antioxidant-UV-absorber have been synthesized by two-step controlled isocyanation of stabilizing function compounds. (2) Monomeric stabilizers have been prepared by direct isocyanation of stabilizing functional compounds (TMP, PMP, ATMP, DHBP, DTHMP) with unsaturated isocyanates (*m*-TMI, AI) and two-step controlled isocyanation of diisocyanate with unsaturated acid (acylic acid, methyl methacrylic acid) and HA (TMP, PMP, ATMP), DHBP, DTBHP or by addition reaction of amino-piperidine to unsaturated epoxide. (3) Polymeric stabilizers have been prepared by copolymerization of monomeric stabilizers with vinyl monomers and hydrosilylation of monomeric stabilizers; while macro-molecular functional reaction of stabilizing functional compounds is a very useful route for preparing polymeric stabilizers with optimal M_w .

REFERENCES

- 1 Rabek, J.F., "Photostabilization of Polymer", Elsevier, Applied Science Publisher, New York, 1990
- 2 Pan, J.Q., Polymer Bulletin, 1992 (3): 138
- 3 Lau, W.W.Y. and Pan, J.Q., "Polymeric Light Stabilizers and Antioxidants", in "Desk Reference of Functional Polymer", ed. by Arshady, R., ACS Press, New York, 1996, p.621
- 4 Lau, W.W.Y. and Pan, J.Q., J. Institute of Engineering (Singapore), 1995, 35(3): 31
- 5 Lau, W.W.Y. and Pan, J.Q., "Preparation, Characterization and Performance of New Light Stabilizers", in "The Proceeding of Polymer Stabilizers, Modifiers Conference", ACS, Hilton Head Island, South Carolina, 1997, p.150
- 6 Lau, W.W.Y. and Pan, J.Q., "Hindered Amine Light Stabilizers, Monomers", in "Polymeric Materials Encyclopedia", ed. by Salamone, J.C., CRC Press Inc., New York, 1996, Vol.5, p.3054
- 7 Minagawa, M., Polym. Degrad. Stab., 1989, 25: 121
- 8 Gugumus, F., Polym. Degrad. Stab., 1989, 24: 289
- 9 Padron, A.J.C., J. Macromol. Sci. Rev. Chem., 1990, C3: 107
- 10 Gugumus, F., Polym. Degrad. Stab., 1994, 44(2): 273
- 11 Kikkawa, K., Polym. Degrad. Stab., 1995, 49(1): 135
- 12 Pan, J.Q., Yang, Z., Zhang, T., Lau, W.W.Y. and Lee, C.S., Polym. Degrad. Stab., 1994, 40: 85
- 13 Pan, J.Q., Lau, W.W.Y., Zhang, Z. and Hu, X., Polym. Degrad. Stab., 1996, 53(2): 153
- 14 Lau, W.W.Y. and Pan, J.Q., Polym. Degrad. Stab., 1998, 60(2-3): 459
- 15 Pan, J.Q. and Lau, W.W.Y., J. Macromol. Sci. Rev., Macromol. Chem. Phys., in press
- 16 Pospisil, J., Polym. Degrad. Stab., 1995, 49(1): 99
- 17 Pan, J.Q. and Lau, W.W.Y., J. Institute of Engineering (Singapore), in press
- 18 Pan, J.Q., Liu, N.C. and Lau, W.W.Y., Polym. Degrad. Stab., 1998, 62: 165
- 19 Liu, N.C., Pan, J.Q. and Lau, W.W.Y., Polym. Degrad. Stab., 1998, 62: 307
- 20 Pan, J.Q., Lau, W.W.Y., Lin, J. and Tan, K.L., Polym. Degrad. Stab., 1994, 46: 45

- 21 Pan, J.Q., Lau, W.W.Y., Lin, J. and Tan, K.L., *Polym. Degrad. Stab.*, 1994, 46: 51
- 22 Pan, J.Q., Lau, W.W.Y., Lin, J., Tan, K.L. and Goh, S.H., *Polym. Degrad. Stab.*, 1995, 49(2): 231
- 23 Pan, J.Q., Lau, W.W.Y. and Lin, J., *Polym. Degrad. Stab.*, 1995, 49(3): 379
- 24 Pan, J.Q., Liu, N.C. and Lau, W.W.Y., *Polym. Degrad. Stab.*, 1998, 62: 315
- 25 Liu, N.C., Pan, J.Q. and Lau, W.W.Y., *Polym. Degrad. Stab.*, 1999, 63: 71
- 26 Pan, J.Q., Chen, W., Song, Y. and Hu, X., *Polym. Degrad. Stab.*, 1993, 39(1): 85
- 27 Pan, J. Q., Lau, W.W.Y., Zhang, Z. and Hu, X., *J. Appl. Polym. Sci.*, 1996, 61: 1405
- 28 Lau, W.W.Y., Lee, C.S., Goh, S.H., Lee, S.Y., Pan, J.Q. and Song, Y., *J. Appl. Polym. Sci.*, 1993, 50(3): 403
- 29 Pan, J.Q., Queck, P.W., Liu, N.C. and Lau, W.W.Y., *J. Appl. Polym. Sci.*, 2000, 78: 403
- 30 Pan, J.Q., Lau, W.W.Y. and Lee, C.S., *J. Polym. Sci. Chem.*, 1994, 32(5): 997
- 31 Pan, J.Q., Liu, N.C. and Lau, W.W.Y., "New Polymeric Stabilizers", in "Proceeding of the 4th National Symposium on Progress in Materials Research", Institute of Materials Research and Engineering, Singapore, 1998, p.247
- 32 Pan, J.Q., Zhou, X., Wu, Y., Ma, Z. and Zhao, R., *Acta Polymerica Sinica*, 1987, (3): 234