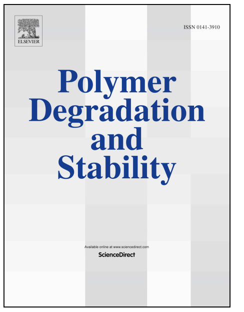
Accepted Manuscript



Efficiency and mechanism for the stabilizing action of *N,N'*-bis(phenylcarbamoyl)alkyldiamines as thermal stabilizers and co-stabilizers for poly(vinyl chloride)

Si Chen, Xiaopeng Xu, Jiahuan Zhang, Wei Tang, Yingjun Qu, Xu Wang

PII: S0141-3910(14)00149-9

DOI: 10.1016/j.polymdegradstab.2014.04.003

Reference: PDST 7308

To appear in: *Polymer Degradation and Stability*

Received Date: 28 February 2014

Revised Date: 2 April 2014

Accepted Date: 5 April 2014

Please cite this article as: Chen S, Xu X, Zhang J, Tang W, Qu Y, Wang X, Efficiency and mechanism for the stabilizing action of *N,N'*-bis(phenylcarbamoyl)alkyldiamines as thermal stabilizers and co-stabilizers for poly(vinyl chloride), *Polymer Degradation and Stability* (2014), doi: 10.1016/j.polymdegradstab.2014.04.003.

Efficiency and mechanism for the stabilizing action of *N,N'*-bis(phenylcarbamoyl)alkyldiamines as thermal stabilizers and co-stabilizers for poly(vinyl chloride)

Si Chen[a], Xiaopeng Xu[a], Jiahuan Zhang[a], Wei Tang[b], Yingjun Qu[b], Xu Wang[a,*]

[a] College of Chemical Engineering and Materials, Zhejiang University of Technology, Hangzhou 310014, PR China

[b] Zhejiang Himpton New Material Co. , Ltd. , Hangzhou 311113, PR China

ABSTRACT

A series of novel ureido organic stabilizers for poly(vinyl chloride) (PVC) with different length of alkyl chains, including *N,N'*-bis(phenylcarbamoyl)ethylenediamine (NA2), *N,N'*-bis(phenylcarbamoyl)butylenediamine (NA4) and *N,N'*-bis(phenylcarbamoyl)hexamethylenediamine (NA6) were designed and synthesized, which have greater stabilizing efficiency compared with Ca/Zn stabilizers and phenylurea at the same concentration in PVC mixtures. The results of Congo red test, discoloration test, thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectra showed that the ureido moieties of NAn (n=2, 4, 6) have stronger ability to replace the labile chlorine atoms in PVC chains, but weaker ability to absorb hydrogen chloride (HCl) than those in phenylurea. On the other hand, longer alkyl chains in the synthesized organic stabilizers had positive effect in stabilizing efficiency for PVC, which was proved by the results that NA6 was the most efficient stabilizer among the present study, followed by NA4 and NA2. Furthermore, mixing the model compound NA6 with zinc stearate in different mass ratios led to a true synergistic effect, the

*Corresponding author. Tel./fax: +86 0571 88320855
E-mail address: wangxu@zjut.edu.cn (X. Wang)

"zinc burning" of PVC products was remarkably postponed.

Key words: Poly(vinyl chloride), *N*,*N'*-bis(phenylcarbamoyl)alkyldiamines, Organic thermal stabilizer, Stabilization mechanism, Synergistic effect

1. Introduction

As the most important additives for poly(vinyl chloride) (PVC), thermal stabilizers must be incorporated to restrain the thermal degradation resulted from inherent structural defects in the polymer chains during thermal processing [1-4]. It is generally accepted that thermal stabilizers realize the thermal stability mainly through absorption of hydrogen chloride (HCl) released by the degradation of PVC or reacting with the labile chlorine atoms, such as allylic and tertiary chlorine atoms [5-7]. At present, the main commercial stabilizers used for PVC include lead salts [8], organotin compounds [9], metal soaps [10], and organic stabilizers [11]. Although lead salts and organotin compounds have high efficiency to stabilize PVC, they are restrained due to their toxicity. In respect of the increasing public awareness of environmental issues in the world, the performance contribution of metal soaps and organic stabilizers has become increasingly important [12,13].

Urea derivatives have been widely investigated as organic stabilizers for PVC during the last few decades [14-16]. However, application of urea derivative stabilizers is limited because of their low efficiency. Hence, the attention of many investigators has been focused on exploring new kinds of urea derivative stabilizers which can meet the demands of PVC industry. A series of phenylurea and phenylthiourea derivatives developed by Sabaa et al. [17-19], revealed high stabilizing potency for PVC and led to a true synergistic effect with metal soaps. Uracil derivatives, which could be synthesized using urea derivatives as raw materials, have been proved to be effective additives for stabilization of PVC against thermal degradation in our previous study [20].

Herein, a class of *N,N'*-bis(phenylcarbamoyl)alkyldiamines (NAn, n=2, 4, 6) were synthesized, characterized and investigated as novel organic thermal stabilizers for PVC. The influence of the alkyl chain length of these compounds on stabilizing efficiency for PVC was investigated and the results suggested that longer alkyl chains had positive effect in stabilizing efficiency for PVC. In addition, by using them as co-stabilizers with zinc stearate, they had special postponing “zinc burning” effect of PVC products through reacting with the zinc chloride. Congo red test, discoloration test, thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectra were used to systematically discuss the mechanism for the stabilizing action of the synthesized organic stabilizers.

2. Experimental

2.1. Materials

PVC (SG-5, average degree of polymerization: 1000) used in this work was purchased from Xinjiang Tianye (Group) Co. Ltd., China. Calcium stearate ($CaSt_2$, calcium content: 6.6-7.4%), zinc stearate ($ZnSt_2$, zinc content: 10-12%) and dioctyl phthalate (DOP, C.P.) and $CaCO_3$ (1000 mesh) were supplied by Zhejiang Himpton New Material Co. Ltd., China. $CaSt_2$/$ZnSt_2$ thermal stabilizers (Ca/Zn) consisted of $CaSt_2$ (50 wt%) and $ZnSt_2$ (50 wt%). Phenylurea (PU, A.R.) was purchased from

Aladdin Reagent, China. Other chemical reagents used in this study are of analytical grade.

2.2. Preparation of *N,N'*-bis(phenylcarbamoyl)alkyldiamines

N,N'-bis(phenylcarbamoyl)alkyldiamines were all prepared according to the following methods: phenylurea (5mmol) and alkyldiamines (10mmol) were dissolved in 25 mL 1,4-dioxane in a 100 mL round-bottomed flask, equipped with a magnetic stirrer and a thermometer. The mixture was then stirred and heated to reflux for about 24 h under an argon atmosphere. After the reaction, the resultant solid was separated by filtration, washed with deionized water, recrystallized using methanol, and dried in a vacuum desiccators at 50℃ for 12 h.

2.3. Characterization

^{1}H-NMR spectra of the synthesized stabilizers were measured on an ANANCEIII (500 MHz) spectrometer (Bruker Corporation, Switzerland), using DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard.

Mass spectra of the synthesized stabilizers were recorded on a 6210 TOF LC/MS mass spectrometer (Agilent, USA) by positive mode electrospray ionization.

Thermal degradation of the synthesized stabilizers were measured on a SDT Q600 thermogravimetric analyzer (TGA) (TA Instruments., USA) from room temperature to 700℃ at a heating rate of 10℃/min in a nitrogen atmosphere.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrophotometer (Thermo Fisher Scientific Inc., USA) by KBr disc method.

2.4. Preparation of PVC samples

PVC resin (100 phr), DOP (15 phr), $CaCO_3$ (10 phr) and stabilizers (2 phr) were mixed thoroughly in a mortar, and the obtained compound was processed into sheets with an approximate thickness of 1.0 mm on an open twin-wheel mill (LRM-S-150/3E, Labtech Ltd., Sweden) for 5 min at 180℃. The thermal stability of prepared PVC sheets was determined by discoloration test and thermogravimetric analysis.

2.5. Evaluation of stabilizing efficiency

2.5.1. Congo red test

The PVC compound mixed with 2 phr stabilizers in the mortar was put into a tube with Congo red test paper located at 2 cm above the sample. The tube was immersed into an oil bath at 180℃ in air for evaluating static thermal stability of PVC compound. The static thermal stability time (T_s) was defined as the time when the Congo red paper began to turn to blue.

2.5.2. Discoloration test

The PVC sheets were cut into about 30 mm × 20 mm strips and heated in a temperature-controlled oven (DHG-9140A, Shanghai Yiheng Scientific instruments Co.,Ltd., China) at 180℃ in air. Strips were taken out of the oven every 10 min and subjected to visual examination using a scanner (Bizhub 283, Konica Minolta, Int. Japan). The effect of the stabilizers was evaluated by the comparison of visual color differences of the heated PVC strips.

2.5.3. Thermogravimetric analysis

Thermal degradation of the PVC sheets were measured on a thermogravimetric analyzer (SDT Q600, TA Instruments., USA) from room temperature to 700℃ at a heating rate of 10℃/min in a nitrogen atmosphere.

3. Results and discussion

3.1 Characterization of NAn

The structures of NAn were identified by ^{1}H-NMR spectra and mass spectra.

N,N'-bis(phenylcarbamoyl)ethylenediamine (NA2, as shown in Fig 1): White solid, yield: 75%. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ_a= 3.19(t, 4H), δ_b=6.19 (s, 2H), δ_f= 6.88(t, 2H), δ_e= 7.19(t, 4H), δ_d= 7.38(d, 4H), δ_c= 8.52(s, 2H). MS m/z: 299.1[M+H]$^+$, m/z: 321.1[M+Na]$^+$.

N,N'-bis(phenylcarbamoyl)butylenediamine (NA4, as shown in Fig 2): White solid, yield: 61%. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ_a= 1.45(s, 4H), δ_b=3.11 (d, 4H), δ_c= 6.13(t, 2H), δ_g= 6.88(t, 2H), δ_f= 7.19(t, 4H), δ_e= 7.38(d, 4H), δ_d= 8.37(s, 2H). MS m/z: 327.2 [M+H]$^+$, m/z: 349.2 [M+Na]$^+$.

N,N'-bis(phenylcarbamoyl)hexamethylenediamine (NA6, as shown in Fig 3): White solid, yield: 54%. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ_a= 1.45(s, 4H), δ_b= 3.09 (d, 4H), δ_c= 6.13(t, 2H), δ_g= 6.87(t, 2H), δ_f= 7.21(t, 4H), δ_e= 7.37(d, 4H), δ_d= 8.37(s, 2H). MS m/z: 355.2 [M+H]$^+$.

The thermal behavior of the synthesized stabilizers at a constant heating rate of 10℃/min was characterized by TGA. The temperature of the rapidest decomposition (T_{rpd}) and residue yield at 200℃ obtained for these stabilizers are summarized in Table 1. As listed in Table 1, all of the synthesized stabilizers are relatively stable at temperature up to 200℃ with a weight loss less than 0.4% and the T_{rpd} occurred over

240℃. The results reveal that NAn are stable at the processing temperature range of 160-200℃ in PVC system and therefore could be used as thermal stabilizers for PVC.

3.2 Thermal stability of NAn stabilized PVC

Results of the thermal stability against the dehydrochlorination process of PVC containing NAn evaluated by Congo red test are shown in Fig.4. The results of PVC samples stabilized by Ca/Zn stabilizers (Ca/Zn) and phenylurea (PU) used as reference stabilizers are also given for comparison. It is seen that these three investigated organic stabilizers exhibit similar stabilizing efficiency in stabilization of PVC and show greater stabilizing efficiency than Ca/Zn. However, from the stability times, it appears that phenylurea (PU) is more efficient than NAn as thermal stabilizers for PVC. PU is likely to act as a stronger hydrogen chloride (HCl) scavenger than NAn. This is because the $-NH_2$ group in PU has a higher activity to react with HCl than the $-NH-CH_2-$ group in NAn [16]. It is well known that the degradation process of PVC is initiated by the structural defects in the polymer and could be accelerated by the HCl released in the degradation process [2]. Absorption of HCl is the secondary stabilizing function of a stabilizer for PVC because it does not stop the degradation process completely, but reduces the degradation rate [21].

Fig. 5 shows the results of the discoloration tests on PVC stabilized by different thermal stabilizers at 180℃ in air. It is shown that the PVC strips containing Ca/Zn has a good initial color, but turns black suddenly at 40 min because of the disadvantages of Ca/Zn stabilizers in long-term stability known as “zinc burning” effect [22]. Compared with Ca/Zn, PVC strips stabilized with these four urea derivative stabilizers exhibit significant improvements in long-term stability. As far as the initial color is concerned, all the PVC strips stabilized with NAn shows better initial colors than PVC strip stabilized with PU, and particularly NA6 exhibits best performance among these five stabilizers. This fact suggests that NAn, when compared to PU, have stronger ability in replacing the labile chlorine atoms to interrupt the formation of conjugated double bonds in PVC chains from the early stage of degradation, since the formation of these bonds could lead to the discoloration of PVC. Influenced by the alkyl chains, the ureido moieties of NAn have high activity to react with the labile chlorine atoms in PVC chains. In the case of PVC strips stabilized with NAn, there is an improvement in stabilizing efficiency with increasing the length of alkyl chains in NAn. With a longer alkyl chain, NA6 may have better compatibility with PVC and therefore is easier to be dispersed in PVC to react with the labile chlorine atoms during thermal processing, so explaining its high efficiency as a stabilizer [23].

3.3 Thermogravimetric analysis of NAn stabilized PVC

The TGA curves of PVC stabilized with different thermal stabilizers are shown in Fig. 6. It is observed that PVC thermally degrades in two steps, the first of which is mainly related to dehydrochlorination with subsequent formation of conjugated polyenes, and the second one includes the pyrolysis of polyenes, structural changes, crystallization, isomerization, crosslinking and aromatization [24].

Table 2 gives the thermogravimetric data for PVC stabilized with NAn compared with those for PVC stabilized with Ca/Zn and PU. It could be found that when using

NAn as stabilizers, the temperatures of onset decomposition (T_s) occurred at higher values of temperature than Ca/Zn and PU and the sample containing NA6 shows the highest T_s among the five samples. These data conform to the results of the discoloration tests. This fact suggest, once more, that NAn are high efficiency thermal stabilizers for PVC, and NA6 is the most efficient stabilizer among the present study, followed by NA4 and NA2. As far as the weight loss of the first step (W_f) is concerned, these three investigated organic stabilizers show lower values than Ca/Zn, but higher than PU. Since HCl is the main volatile product of the first step, it is clear that PU could absorb higher amount of HCl than NAn and Ca/Zn during the processing of PVC. These results of TGA are in good accordance with the analysis of Congo red test.

3.4. Thermal stabilizing mechanism of NAn

This section deals with a study oriented towards the mechanism of NAn stabilizing PVC. Further experiments were carried out with a view to suggest a possible mechanism which could explain the stabilizing efficiency of NAn. The model organic stabilizer NA6 was subjected to a stream of HCl gas at 180℃ in air for 2 h, and the product was heated at 120℃ in air for 4 h to remove the residual HCl. Then the treated product was added into deionized water, and the relevant mixture was filtered. A white precipitate was generated in the clear filtrate when one droplet of 0.1 N silver nitrate solution was added in. This indicated the presence of chloride ions in the filtrate, and further confirmed that NA6 could react with HCl at 180℃ [22]. However, the FTIR spectrum of NA6 after treatment is found to be almost identical to that of the original untreated sample (Fig. 7), indicating that NA6 reacts with HCl through an acid-base interaction but not chemical bonds [25]. From the aforementioned experiments, a probable mechanism of the HCl scavenging action of NA6 is proposed and described in Fig. 8. However, it was reported by Sabaa et al. [17] that the FTIR spectrum of phenylurea, which was subjected to a stream of HCl at 180℃ in air for 30 min, showed a new band at 682.8 cm^{-1} corresponding to C-Cl bond. In addition to acid-base interaction, phenylurea reacts with HCl by the chemical bonding, so explaining its higher efficiency than NAn in absorbing HCl.

Another experiment was performed to investigate whether NAn could replace the labile chlorine atoms in PVC chain. The NA6 stabilized PVC was mixed on an open twin-wheel mill (LRM-S-150/3E, Labtech Ltd., Sweden) for 10 min at 180℃. Then NA6 stabilized PVC was dissolved in tetrahydrofuran and the mixture was separated by filtration to remove the unreacted NA6. Finally, the PVC sample was precipitated with methanol and collected by filtration. Fig. 9 shows the FTIR spectrum of this purified PVC sample, and the FTIR spectrum of pure PVC is also given for comparison. The FTIR chart of the purified sample shows an intense peak at 3326.3 cm^{-1} can be assigned to the stretching of the N-H bonds. The peaks at 1629.9, 1596.9 and 1563.7 cm^{-1} can be attributed to the characteristic absorption of the benzene, and the peak 1720.2 cm^{-1} is corresponding to the absorption of C=O bonds stretching [26]. These facts indicate that NA6 become chemically bonded to the degraded polymeric chains during the stabilization process.

From the aforementioned results, a probable mechanism of stabilizing action of NA6 is proposed and described in Fig. 10. According to the mechanism, the labile chlorine atom (allylic chlorine) is detached from the PVC chain in the form of a chloride anion leaving a carbocation on the polymer chain [Eq. (1)]. The detached chlorine anion, which is a weak base and the only nucleophile in the system, can easily attack the C=N double bond of the enol form of the stabilizer molecule [17], and leaving a negative charge on the nitrogen atom [Eq. (3)]. Once the stabilizer anion is formed, it is attached to the carbocation on the PVC chain, thus the labile chlorine atom is replaced by a relatively more stable NA6 moiety [Eq. (4)].

3.5. Co-stabilizing effectiveness of NAn and $ZnSt_2$

Ca/Zn stabilizers, the mainly used metal soaps, are more acceptable for PVC stabilization in PVC industry because of their nontoxic and cheap [10]. However, Ca/Zn stabilizers have some disadvantages in long-term stability due to the marked ‘‘zinc burning’’ effect, and therefore cannot be used singly [22]. It has been reported that Ca/Zn stabilizers have synergistic effect with some nitrogen-containing organic stabilizers and present favorable stabilization [13-19]. A combination of NAn with Ca/Zn stabilizers is expected to produce synergistic stabilization effect to PVC. In this section, the model compound NA6 is investigated as a co-stabilizer with $ZnSt_2$ for PVC by the discoloration test.

The results of the discoloration tests on PVC strips containing NA6/$ZnSt_2$ and $CaSt_2$/$ZnSt_2$ stabilizers in different mass ratios are shown in Fig. 11(a) and (b), respectively. It is shown that PVC strip containing $ZnSt_2$ alone exhibits excellent initial color, but turn black completely within 10 min. This is because the production of the stabilizing reaction is $ZnCl_2$ which can result in a sudden “zipper dehydrochlorination" of PVC. However, the combination of NA6 and $ZnSt_2$ greatly extends the long-term stability of PVC strips. It is seen in Fig. 11(a) that the blackening time of PVC strips are promoted by increasing the mass ratios of NA6/$ZnSt_2$ from 0/2 to 1.6/0. NA6/$ZnSt_2$ stabilizers in mass ratio of 1.2/0.8 exhibit a maximized synergistic effect with both acceptable initial color and long-term stability for PVC products. Furthermore, compared with the PVC strips stabilized by $CaSt_2$/$ZnSt_2$, the strips containing NA6/$ZnSt_2$ exhibit better initial color and show better long-term stability. The highly synergistic effect of NA6/$ZnSt_2$ could be attributed to the reaction between NA6 and $ZnCl_2$. As is shown in Fig. 12, NA6 can act as an acceptor or chelating agent for $ZnCl_2$ by forming an inert complex to retard the sudden "zipper dehydrochlorination" of PVC.

4. Conclusion

N,*N'*-bis(phenylcarbamoyl)alkyldiamines have been investigated as organic thermal stabilizers for PVC. The stabilizing efficiency of these compounds were measured by Congo red test, discoloration test and thermogravimetric analysis. As organic thermal stabilizers *N*,*N'*-bis(phenylcarbamoyl)alkyldiamines show better thermal stabilizing performance than Ca/Zn stabilizers and phenylurea. The mechanism of stabilizing action of these compounds is also proposed. *N*,*N'*-bis(phenylcarbamoyl)alkyldiamines may replace the labile chlorine atoms to interrupt the formation of conjugated double bonds in PVC chains, and act as the absorber of hydrogen chloride to restrain the self-catalytic dehydrochlorination.

Combining NA6 with $ZnSt_2$ leads to a remarkable improvement in long-term stability for PVC products. NA6/$ZnSt_2$ stabilizers in mass ratio of 1.2/0.8 exhibit a maximized synergistic effect with both acceptable initial color and long-term stability for PVC products. The highly synergistic effect of NA6/$ZnSt_2$ could be attributed to the reaction between NA6 and $ZnCl_2$. NA6 can act as an acceptor or chelating agent for metal chloride by forming an inert complex to retard the sudden "zipper dehydrochlorination" of PVC.

Acknowledgments

Financial support from the National Natural Science Foundation of China (Grant No: 21004052, 51173167) and the Opening Foundation of Zhejing Provincial Top Key Discipline (Grant No: G9713101008) are gratefully acknowledged.

References

[1] Starnes Jr WH. Structural and mechanistic aspects of the thermal degradation of poly(vinyl chloride). Prog Polym Sci 2002;27:2133–70.
[2] Starnes Jr WH. Structural defects in poly(vinyl chloride). J Polym Sci Part A Polym Chem 2005;43:2451–67.
[3] Starnes Jr WH. Overview and assessment of recent research on the structural defects in poly(vinyl chloride). Polym Degrad Stab 2012;97(9):1815–21.
[4] Moulay S. Chemical modification of poly (vinyl chloride)–still on the run. Prog Polym Sci 2010;35(3):303–31.
[5] Tawfik SY, Asaad JN, Sabaa MW. Thermal and mechanical behaviour of flexible poly(vinyl chloride) mixed with some saturated polyesters. Polym Degrad Stab 2006;91(2):385–92.
[6] Fisch MH, Bacaloglu R. Mechanism of poly(vinyl chloride) stabilisation. Plast Rubber Compos 1999;28:119–24
[7] Liang K, Li R, Liu G. Mechanism and research progress of Ca/Zn compound heat stabilizer. Plast Sci Technol 2009;37(8):76–9.
[8] Kalouskova R, Novotna M, Vymazal Z. Investigation of thermal stabilization of poly(vinyl chloride) by lead stearate and its combination with synthetic hydrotalcite. Polym Degrad Stab 2004;85(2):903–9.
[9] Arkis E, Balkose D. Thermal stabilization of poly(vinyl chloride) by organotin

compounds. Polym Degrad Stab 2005;88(1):46–51.

[10] Fang L, Song YH, Zhu XN, Zheng Q. Influence of lanthanum stearate as a co-stabilizer on stabilization efficiency of calcium/zinc stabilizers to polyvinyl chloride. Polym Degrad Stab 2009;94(5):845–50.

[11] Liu P, Zhu LY, Fang Y, et al. Hydroxylbenzylthioethers as novel organic thermal stabilizers for rigid PVC. Polym Degrad Stab 2007;92(3):503–8

[12] Stipanelov vrandecic N, Klaric I, Roje U. Effect of Ca/Zn stabilizer on thermal degradation of poly(vinyl chloride)/chlorinated polyethylene blends. Polym Degrad Stab 2001;74:203–12.

[13] Sabaa MW, Mohamed RR, Oraby EH. Vanillin–Schiff's bases as organic thermal stabilizers and co-stabilizers for rigid poly(vinyl chloride). Eur Polym J 2009;45(11):3072–80.

[14] Mohamed NA, Yassin AA, Khalil KD, Sabaa MW. Organic thermal stabilizers for rigid poly(vinyl chloride) I. Barbituric and thiobarbituric acids. Polym Degrad Stab 2000;70(1):5–10.

[15] Sabaa MW, Mohamed NA, Khalil KD, Yassin AA. Organic thermal stabilizers for rigid poly(vinyl chloride) II. Benzal thiobarbituric acid and some of its derivatives. Polym Degrad Stab 2000;70(2):121–33.

[16] Mohamed NA, Sabaa MW, Khalil KD, Yassin AA. Organic thermal stabilizers for rigid poly(vinyl chloride) Ⅲ. Crotonal and cinnamal thiobarbituric acids. Polym Degrad Stab 2001;72(1):53–61.

[17] Sabaa MW, Mohamed RR, Yassin AA. Organic thermal stabilizers for rigid poly(vinyl chloride) VIII. Phenylurea and phenylthiourea derivatives. Polym Degrad Stab 2003;81(1):37–45.

[18] Sabaa MW, Mohamed RR, Yassin AA. Organic thermal stabilizers for rigid poly(vinyl chloride) IX. *N*-Benzoyl-*N'*-p-substituted phenylthiourea derivatives. Polym Degrad Stab 2003;81(3):431–40.

[19] Sabaa MW, Mohamed RR, Yassin AA. Organic thermal stabilizers for rigid poly(vinyl chloride). Part X. *N*-acryloyl-*N'*-p-substituted phenylthiourea derivatives. Polym Degrad Stab 2003;82(3):387–93.

[20] Xu XP, Chen S, Tang W, Qu YJ, Wang X. Synthesis and application of uracil derivatives as novel thermal stabilizers for rigid poly(vinyl chloride). Polym Degrad Stab 2012;98(2):659–65.

[21] Xie LH, Li DG, Zhang J. The effect of pentaerythritol-aluminum on the thermal stability of rigid poly(vinyl chloride). J Appl Polym Sci 2013;130(5):3704–9.

[22] Li SM, Yao YW. Effect of thermal stabilizers composed of zinc barbiturate and calcium stearate for rigid poly(vinyl chloride). Polym Degrad Stab 2011;96(4):637–41.

[23] Liu JP, Shang HZ, Zheng YB, Song X. Synthesis and evaluation of poly(dioctyltin maleate-styrene-methyl acrylate) as a stabilizer for poly(vinyl chloride). J Appl Polym Sci 2009;113(2):1216–22.

[24] Gonzalez N, Mugica A, Fernandez-Berridi MJ. Application of high resolution thermogravimetry to the study of thermal stability of poly(vinyl chloride) resins. Polym Degrad Stab 2006;91(4):629–33.

[25] M. Suzuki, H. Saito, H. Shirai, K. Hanabusa. Supramolecular organogel formation triggered by acid–base interaction in two-component system consisting of L-lysine derivative and aliphatic acids. New J Chem 2007;31(9):1654–60.

[26] Luo XZ, Chen ZX, Xiao W. Two-component supramolecular organogels formed by maleic *N*-monoalkylamides and aliphatic amines. J Colloid Interface Sci 2011;362(1):113–7.

Table 1
Thermal properties of NAn

Table 2
TGA results of stabilized PVC

Fig. 1 Structure of *N*,*N'*-bis(phenylcarbamoyl)ethylenediamine (NA2)

Fig. 10 A possible mechanism for the stabilizing efficiency of NA6

Fig. 11 Co-stabilizing effect of NA6 and $ZnSt_2$

Fig. 12 A possible reaction between NA6 and $ZnCl_2$

Fig. 2 Structure of *N*,*N'*-bis(phenylcarbamoyl)butylenediamine (NA4)

Fig. 3 Structure of *N*,*N'*-bis(phenylcarbamoyl)hexamethylenediamine (NA6)

Fig. 4 Stability time of PVC stabilized with different thermal stabilizers processed at 180℃in air.

Fig. 5 Discoloration of PVC stabilized by different thermal stabilizers at 180℃ in air.

Fig. 6 TGA curves of PVC stabilized with different thermal stabilizers.

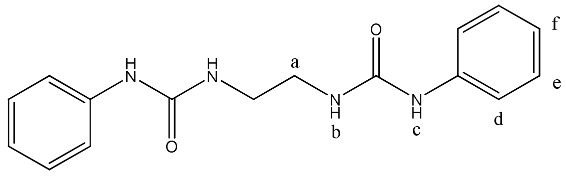
Fig. 7 FTIR spectra of NA6: (a) before treatment (b) treated under HCl gas condition at180℃for 2 h.

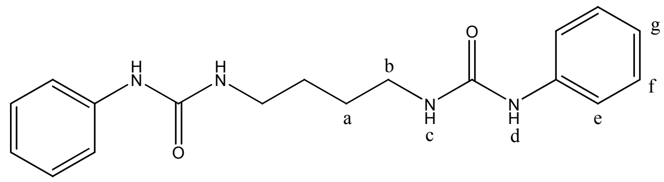
Fig. 8 Mechanism of HCl scavenging.

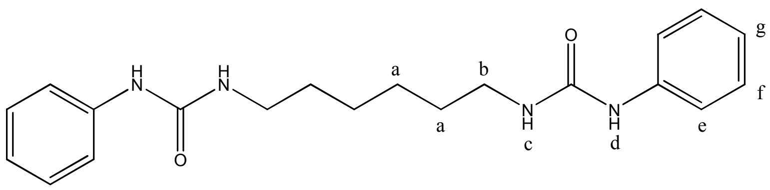
Fig. 9 FTIR spectra of pure PVC (a) and the purified PVC sample (b)

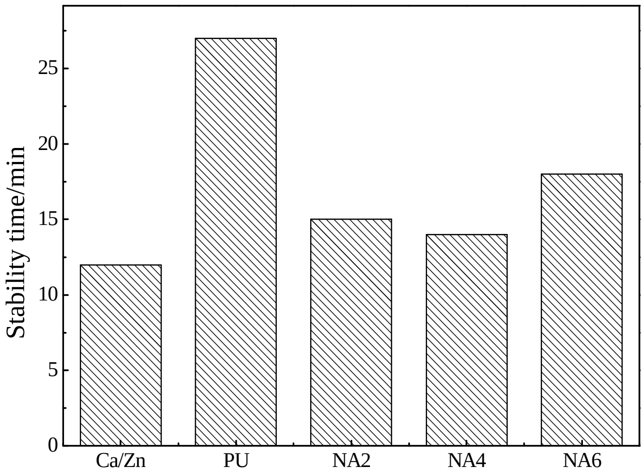
Stabilizers	NA2	NA6	NA6
Weight % at 200℃	99.7	99.8	99.6
T_{rpd} (℃)	307.1	252.5	240.4

Stabilizers	T_s (℃)	W_f(%)
Ca/Zn	197.8	65.7
PU	196.6	61.3
NA2	209.5	62.9
NA4	224.1	63.5
NA6	229.9	63.9

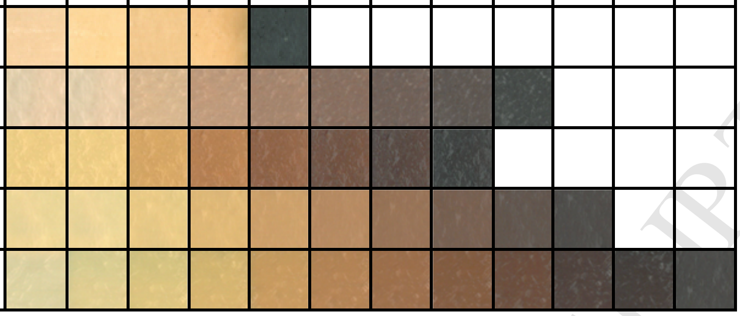

H
H
O
a
N
H
b
O
N
H
c
d
e
f

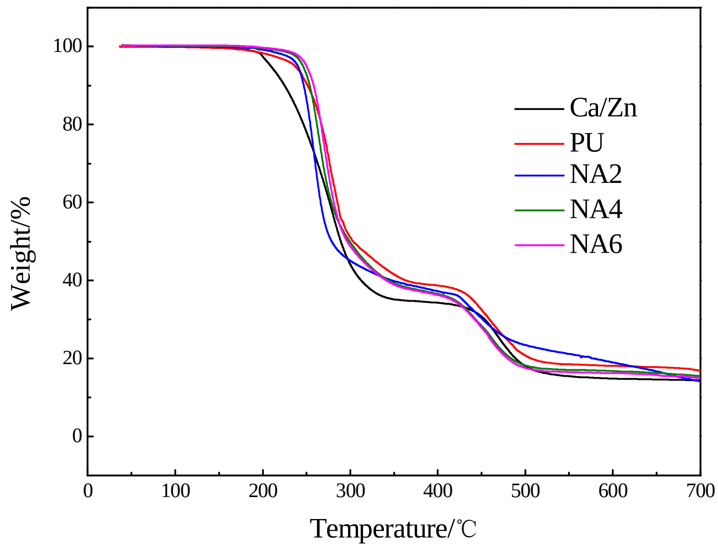

H
N
H
N
O
b
a
O
N
H
c
N
H
d
e
f
g


H
H
a
b
O
g
O
a
N
H
c
N
H
d
e
f

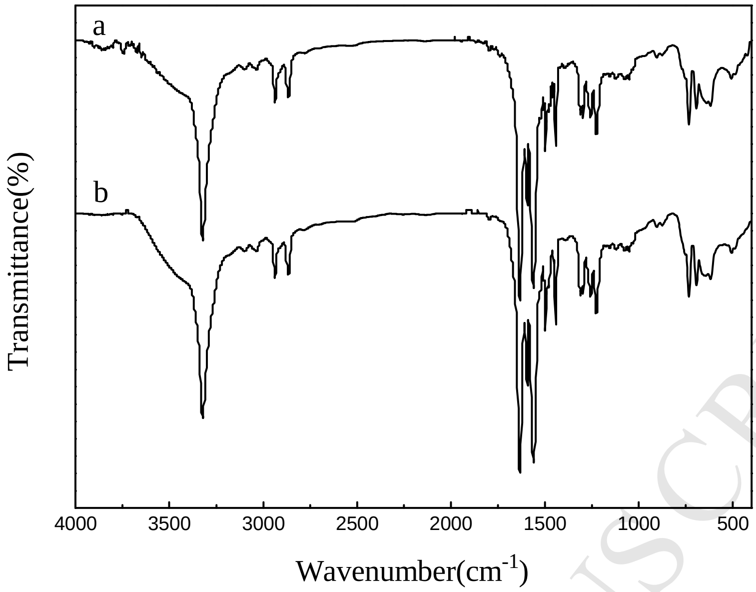

Stability time/min
0
5
10
15
20
25
Ca/Zn
PU
NA2
NA4
NA6

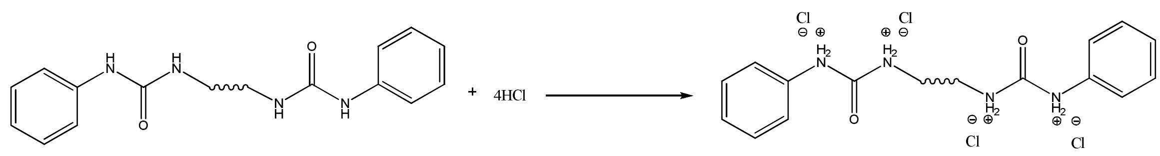
Stabilizer	PVC, 100phr; Stabilizer, 2phr; $CaCO_3$, 15phr; DOP, 10phr											
	Degradation time, ×10min											
	0	1	2	3	4	5	6	7	8	9	10	11
Ca/Zn												
PU												
NA2												
NA4												
NA6												

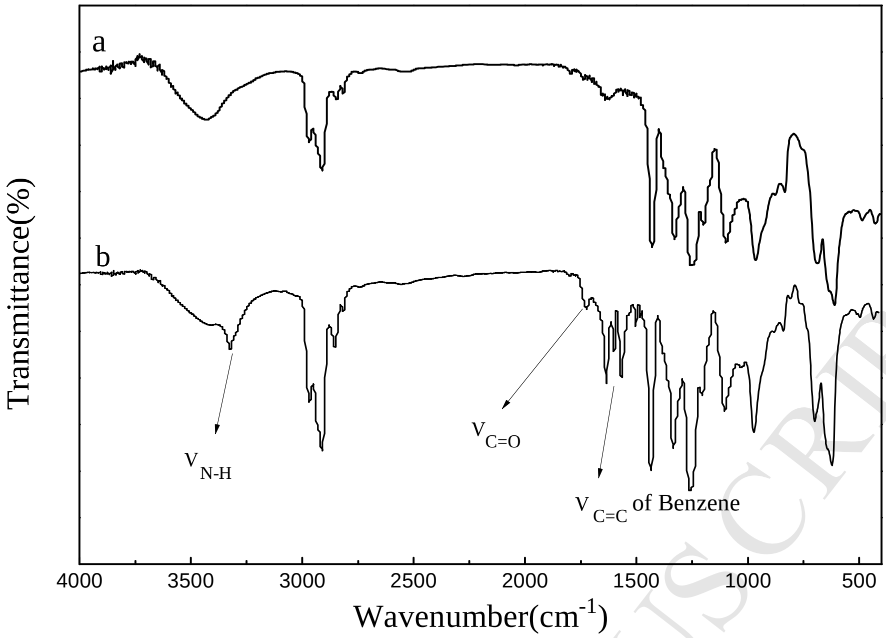


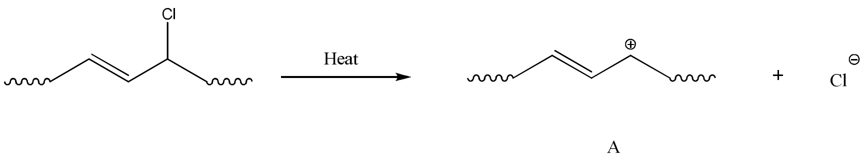


Weight/%
100
80
60
40
20
0
0
100
200
300
400
500
600
700
Temperature/℃
Ca/Zn
PU
NA2
NA4
NA6

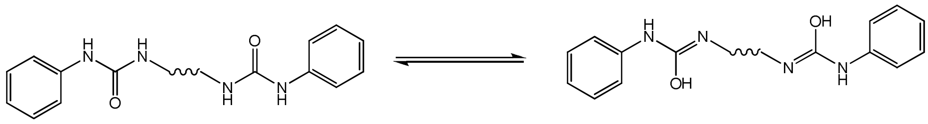

a
b
Transmittance(%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)


H
N
O
H
N
N
H
O
N
H
+
4HCl
Cl
Cl
H2
N
H2
N
O
N
H2
O
N
H2
Cl
Cl

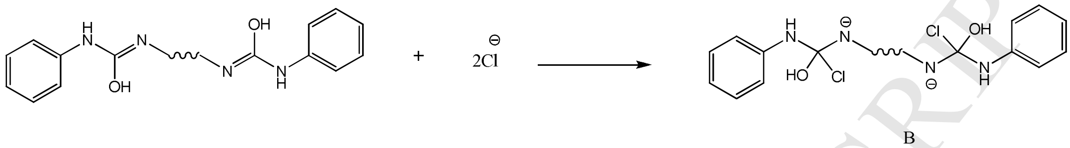

a
b
Transmittance(%)
V N-H
V C=O
V C=C of Benzene
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)



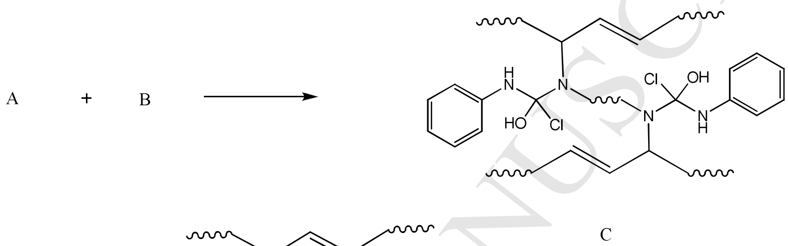
Eq. (1)



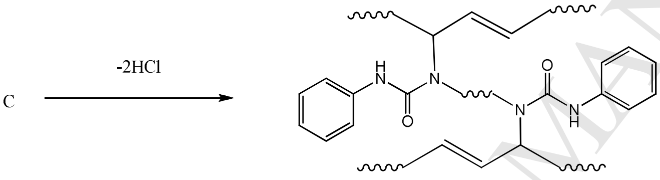
Eq. (2)



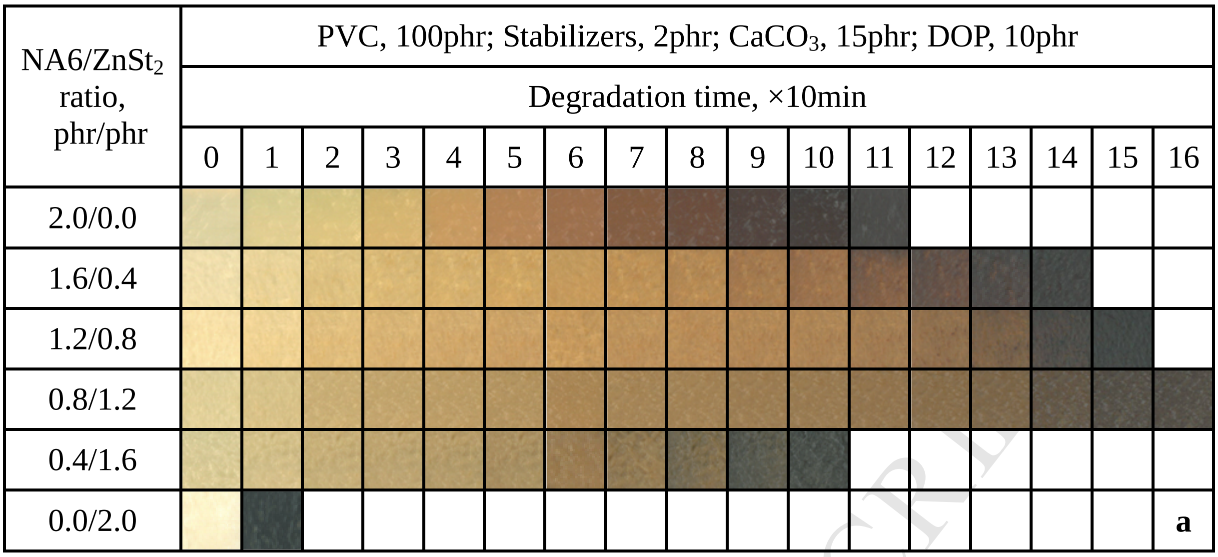
Eq. (3)

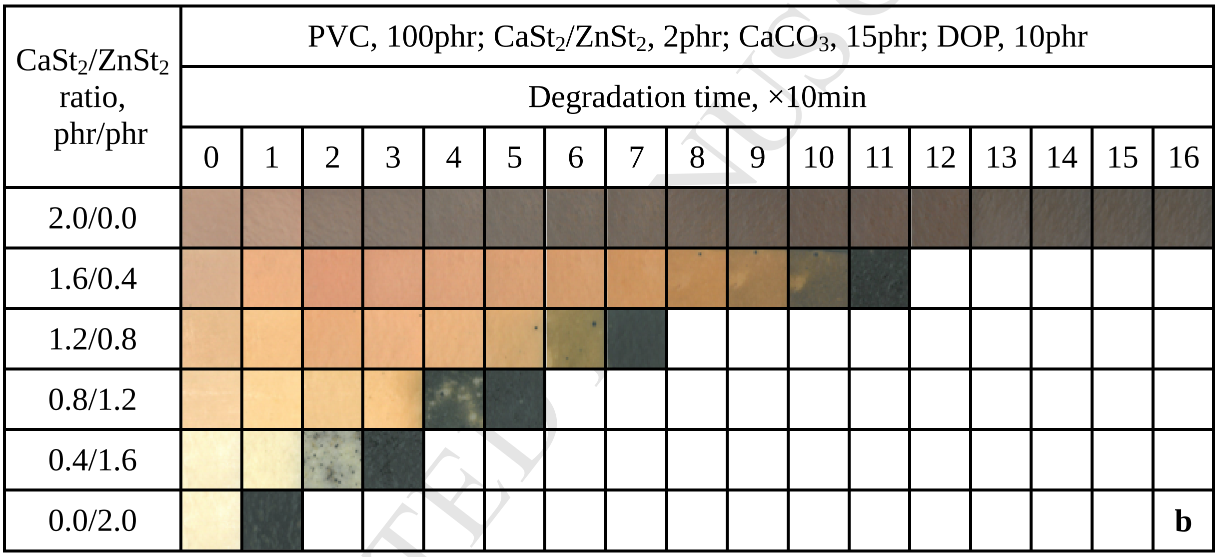


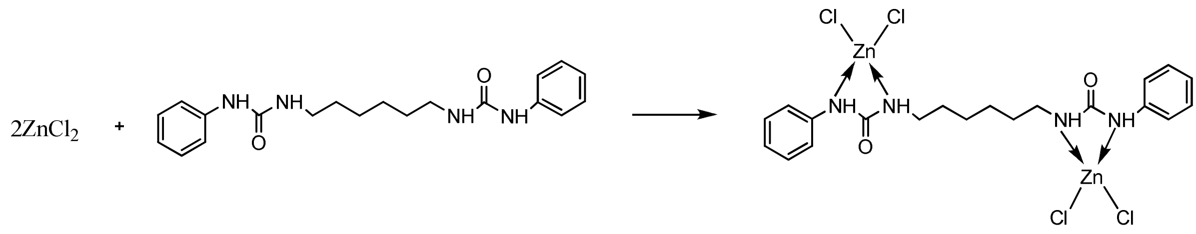
Eq. (4)



Eq. (5)


NA6/ZnSt2 ratio, phr/phr
PVC, 100phr; Stabilizers, 2phr; CaCO3, 15phr; DOP, 10phr
Degradation time, ×10min
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
2.0/0.0
1.6/0.4
1.2/0.8
0.8/1.2
0.4/1.6
0.0/2.0
a


CaSt2/ZnSt2 ratio, phr/phr
PVC, 100phr; CaSt2/ZnSt2, 2phr; CaCO3, 15phr; DOP, 10phr
Degradation time, ×10min
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
2.0/0.0
1.6/0.4
1.2/0.8
0.8/1.2
0.4/1.6
0.0/2.0
b


2ZnCl2
+
NH
NH
O
NH
NH
O
Cl
Cl
Zn
NH
NH
O
NH
NH
O
Zn
Cl
Cl