Synthesis and Evaluation of Poly(dioctyltin maleate-styrene-methyl acrylate) as a Stabilizer for Poly(vinyl chloride)

Jianping Liu,[1,2] Hongzhou Shang,[1] Yubin Zheng,[1] Xia Song[2]

[1]Department of Polymer Science and Materials, Dalian University of Technology, Dalian 116012, China
[2]College of Chemistry and Materials Science, Wenzhou University, Wenzhou 325027, China

ABSTRACT: A novel thermal stabilizer poly(dioctyltin maleate-styrene-methyl acrylate) [P(DOTM-St-MA)] was synthesized by radical solution polymerization with benzene as the solvent and 2,2-azobisisobutyronitrile as the initiator. The structure of terpolymer was characterized by FTIR and ^{1}H-NMR spectra, and thermal stability of the stabilizer was measured by thermogravimetric analysis (TGA). Evaluation of [P(DOTM-St-MA)] as thermal stabilizer for poly(vinyl chloride) (PVC) was measured by acidimeter, and the extent of changing color of PVC was measured by thermal aging method. Compatibilities of four stabilizers with PVC were characterized by scanning electron microscope (SEM). The results showed that, with the same tin content in PVC mixtures, [P(DOTM-St-MA)] exhibited better performance as a PVC stabilizer compared with other stabilizers, such as poly(dibutylin maleate-styrene-methyl acrylate), DOTM, and dibutylin maleate (DBTM). Furthermore, [P(DOTM-St-MA)] had better compatibility with PVC in PVC processing. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1216–1222, 2009

Key words: additives; stabilization; radical polymerization; thermal degradation; PVC

INTRODUCTION

Poly(vinyl chloride) (PVC) is second only to polyethylene (PE) among five kinds of general plastic materials, which was widely used in the industries including architecture, electronic, chemical engineering, packaging, transportation, etc.[1] However, low-thermal stability of PVC leads to hydrogen chloride loss, discoloration, and finally serious corrosion phenomena, accompanied by changes of physical and chemical properties of PVC. Therefore, it is necessary to add some thermal stabilizers to improve the thermal stability of PVC. These plastic additives include metallic soaps,[2–5] organotin compounds,[6–8] organic stabilizers,[9–16] basic lead salts,[17] etc. However, an unavoidable drawback is the volatilization of lower molecular stabilizers during degradation. This can cause poisoning of operators and environmental pollution. Furthermore, it reduces the utilization rate of stabilizers.

Polymeric organotins were upcoming thermal stabilizers becasue of its improving compatibility between PVC and stabilizers, decreasing evaporability, preventing transference, and reducing toxicity and pollution. There have been three methods reported to synthesise polymeric organotins: (1) condensation methods,[18] including organotin polyester, polyether, and polythioether[19–22]; (2) homopolymerization or copolymerization of unsaturated organotin,[23–26] comonomers including styrene (St), unsaturated carboxylic ester, and unsaturation organotin; (3) copolymerization of vinyl chloride and unsaturated organotin.[27]

Radical copolymerization of St, dioctyltin maleate (DOTM), and methyl acrylate (MA) has been carried out. One of the goals of this article was to characterize the terpolymer and evaluate its thermal stability as a novel thermal stabilizer of PVC.

EXPERIMENTAL

Materials and reagents

DOTM with melting point at 106–107°C and tin content at 25.93% was prepared. Methyl acrylate was obtained from Jiangsu Yonghua Fine Chemicals (Jiangsu, China), and St was purchased from Xilong Chemical Factory (Guangxi, China). The comonomers were refined to remove polymerization inhibitors. 2,2′-Azobisisobutyronitrile (AIBN), as an initiator supplied by Shanghai No. 4 Reagent & H.V. Chemical (Shanghai, China), was recrystallized with ethanol. Poly(dibutylin maleate-styrene-methyl acrylate) [P(DBTM-St-MA)] and DBTM were prepared in the laboratory. PVC (S-65) was purchased from Formosa Industries (Taiwan, China). Dioctyl phthalate (DOP),

as a plasticizer, was obtained from Hangzhou Nature Organic Chemicals (Hangzhou, China). $CaCO_3$ (1000 mesh), as a filler, was obtained from Guangxi Hezhou Kelong Micro-powder (Guangxi, China). Other reagents (ACS-grade), used as received, were obtained from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

Terpolymer synthesis

DOTM, St, and MA (mol ratio = 1 : 3 : 1) and 100 mL benzene were added to a three-necked round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser. The reactor was continuously spared with high purity nitrogen to remove any residual oxygen at room temperature, and then 0.3% AIBN was added into the reactor. The polymerization reaction was carried out at $(70 \pm 1)°C$ water-bath for 12 h. The resulting solution was dissolved in the mixed solvent of ethanol and benzene containing a small quantity of hydroquinone and then deposited in methanol. The deposits were collected by filtration, and then washed three times with methanol. The final production was dried at reduced pressure at 60°C until constant weight.

Copolymer characterization

The tin content of terpolymer was measured by IRIS-ICP-AES Advantage Duo inductively coupled plasma atomic emission spectrometer (ICP). The molecular weight distribution of terpolymer was measured by gel permeation chromatography (GPC), with tetrahydrofuran as the solvent. The FTIR spectrum of terpolymer was measured on an EQUINOX55 spectrophotometer, and sample was pressed into KBr pellets. ^{1}H-NMR spectrum was measured on a Bruker Avance 300 NMR spectrometer at room temperature, with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal reference.

TGA of stabilizers were measured on a SDTQ600 integrated thermal-analysis instrument. Nitrogen and calefactive speed were 30 cm^3/min and 10°C/min, respectively.

Preparation of PVC samples

With the same tin content in thermal stabilizers, PVC and thermal stabilizers were mixed with plasticizer, and the mixtures were milled on an open 160B twin-wheel mill at 160°C for 7 min to prepare 1.0-mm thickness PVC films and then cut into 3×2 mm^2 and 30×20 mm^2 rectangular samples. The 3×2 mm^2 samples were used to measure rate of hydrogen chloride liberation, and 30×20 mm^2 samples were used to test PVC discoloration. The compositions of the mixtures are shown in Table I.

Measurements

JSM-6700F Scanning electron microscope (SEM) was used to observe the two-phase interface morphology of PVC films. The samples for SEM were prepared by immersing PVC film in liquid nitrogen and then fractured quickly to get clean surface for SEM test.

According to the standard of ISO182/1-1990, acidimeter was used to measure hydrogen chloride liberation at 200°C.

According to the standard of ASTM-2115-67, the 30×20 mm^2 samples were put in thermal ageing tester at 180°C. Samples were taken out before 10 min and stuck in the order of sampling. Color changes of samples were used to estimate their thermal stability. The WSD-5 whiteness testing system was used to detect changes in whiteness before and after thermal ageing of samples to further evaluate thermal stability of the stabilizers.

RESULTS AND DISCUSSION

Tin content and molecular weight of terpolymer

ICP was used to measure tin content of terpolymer. The result showed that actual value of 12.43% was near to the theoretical value of 13.85%. This indicated that DOTM was involved in copolymerization.

The molecular weight of the terpolymer was measured by GPC, and the testing results were $\overline{M_w} = 79,440, \overline{M_n} = 47,644$ and PD = 1.6674.

TABLE I
The Compositions of Mixture for PVC Samples

Samples	PVC (phr)	DOP (phr)	CaCO$_3$ (phr)	P(DOTM-St-MA) (phr)	P(DBTM-St-MA) (phr)	DOTM (phr)	DBTM (phr)	Lubricant (phr)
A	100	40	30	3.3				0.35
B	100	40	30		2.5	1.2	1	0.35
C	100	40	30					0.35
D	100	40	30					0.35

The samples had the same tin content. DOP expressed a plasticizer and $CaCO_3$ was used as filler.

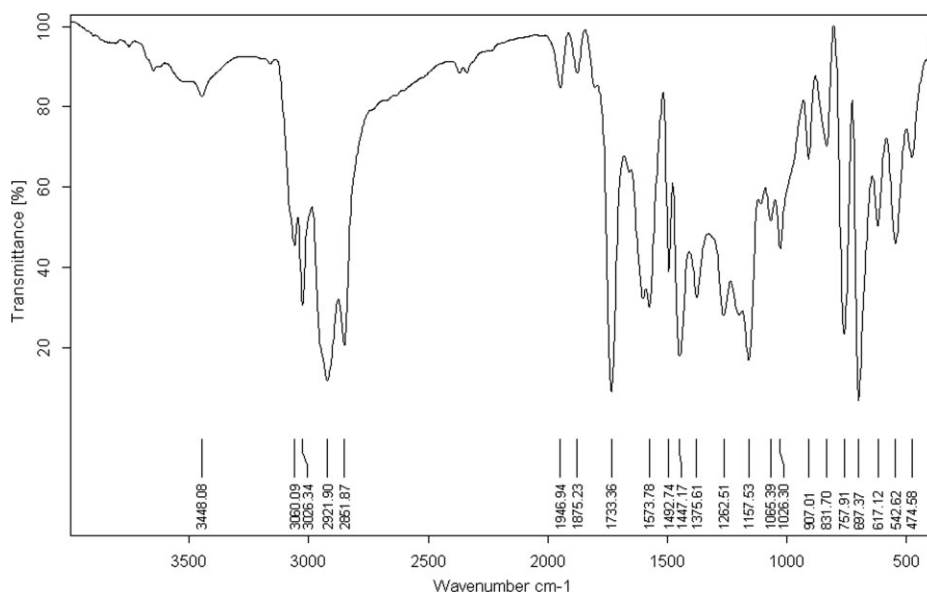**Figure 1** FTIR spectrum of P(DOTM-St-MA).

FTIR and ^{1}H-NMR spectral analysis

FTIR and ^{1}H-NMR spectra were shown in Figures 1 and 2, respectively, which identified the composition of the terpolymer.

On FTIR spectrum (Fig. 1), the peaks at 3060, 3026, 1949, 1573, 1492, 1447, 757, and 697 cm^{-1} were attributed to the characteristic peaks of monosubstituted benzene; The peak at 1733 cm^{-1} was attributed to stretching vibration of —COO of the ester group, and the peaks at 1262 and 1157 cm^{-1} were assigned to stretching vibration of C—O—C of the ester group. The stretching vibration of —CH$_2$— of the octyl group appeared at 2921 and 2851 cm^{-1}, and the bending vibration of —CH$_3$ appeared at 1375 cm^{-1}; the peaks at 617 and 542 cm^{-1} were assigned to the stretching vibration of Sn—C and Sn—O, respectively.

^{1}H-NMR (Fig. 2) spectrum of terpolymer was assigned as follows: the signals at 7.1036–6.6669 ppm were originated to C—H of the benzene ring. The wide signal around at 3.2224 ppm was ascribed to O—CH3 of the ester group. The signals at 2.2212–1.7685 ppm were chemical shifts of Sn—CH$_2$CH$_2$—. The signals at 1.2575 and 0.8729 ppm were regarded as chemical shifts of —CH$_2$CH$_2$— and CH$_3$. ^{1}H-NMR analysis also confirmed the existence of the benzene ring, octyl, and ester groups. Therefore, FTIR and ^{1}H-NMR spectral analysis proved that the terpolymerization was synthesized as expected.

Integral areas, 0.4238 of chemical shifts of CH$_3$ (at 0.8729 ppm), 0.2511of benzene ring (at 7.1036–6.6669 ppm), and 1.2977 of O—CH$_3$ (3.2224 ppm), showed that mol ratio of the three structure units, DOTM, St, and MA, was 1 : 3.68 : 1.19, respectively. Tin content calculated by the intergral area was consistent with the value measured on ICP.

Thermogravimetric analysis of stabilizers

Thermal weight loss was one of the important factors used to evaluate utilization rate and environment pollution of a stabilizer. TGA curves of P(DOTM-St-MA), P(DBTM-St-MA), DOTM, and DBTM were shown in Figure 3. It was obvious that thermal stability of polymeric stabilizers was better than that of low-molecular stabilizers before 350°C. At 160–200°C, which is common PVC processing temperature, weight loss of P(DOTM-St-MA) was 0–1%. However, weight loss of P(DBTM-St-MA), DOTM, and DBTM were 0.5–1.5%, 4–6%, and 5–7% respectively. Furthermore, temperature of P(DBTM-St-MA) with 3% weight loss was 223°C, whereas for P(DOTM-St-MA), its weight loss temperature was up to 280°C. Therefore, P(DOTM-St-MA) was high efficiency thermal stabilizer compared with P(DBTM-St-MA) and other low-molecular weight stabilizers, which greatly improved stability of PVC compound during the process, and reduced or avoided environment pollution due to the volatilization or degradation of auxiliary materials PVC
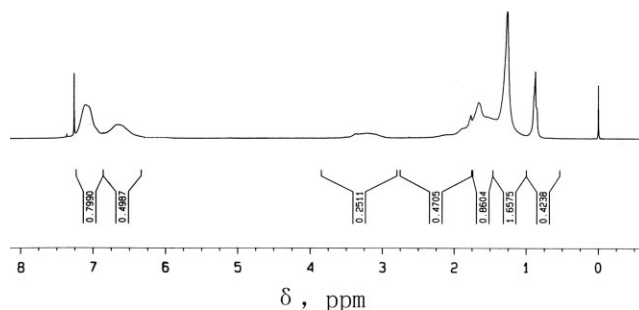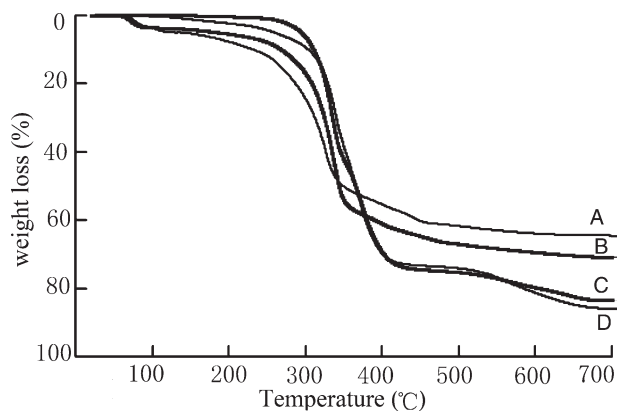

Figure 2 ^{1}H-NMR spectrum of P(DOTM-St-MA).

Figure 3 TGA of stabilizers: (A) DOTM; (B) DBTM; (C) P(DOTM-St-MA); (D) P(DBTM-St-MA).

Figure 4 Amount of liberated HCl from PVC.

processing. However, when temperature was between 350 and 700°C, sequence of weight loss was opposite compare with low temperature area (25–350°C). The reason was that the lower the molecular weight was, the higher the Sn content was, and also the higher the resulting product SnO_2 was. Furthermore, the mass of the residues was in accordance with theoretical calculated values.

Evaluation of stability as thermal stabilizers for PVC

The sheets (5.0 g) with size of 3×2 mm^2 were put into an airtight test tube in 200°C oil-bath. Hydrogen chloride liberated from samples was brought into an absorption pool by high purity nitrogen. An acidimeter with 1% precision was used to measure the liberated amount of HCl, and the results are shown in Figure 4. The releasing speed of HCl measured by an acidimeter showed the abilities of a few stabilizers to restrain thermal degradation, and the abil-
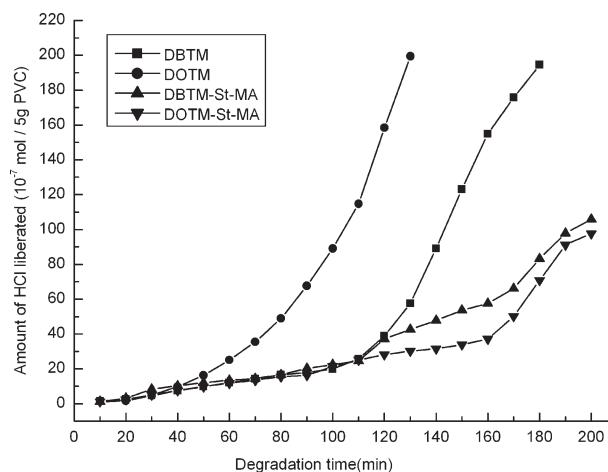
ities from strong to weak ordered as follows: P(DOTM-St-MA) > P(DBTM-St-MA) > DOTM and DBTM. Thermal ageing testing results are shown in Figure 5. Discoloration extent and whiteness values changed with the increase of heating time. This is consistent with the conclusion mentioned earlier.

A consistent conclusion was drawn that P(DOTM-St-MA) is a higher performance stabilizer in comparison with P(DBTM-St-MA) or some traditional low-molecular stabilizers. Polystyrene and poly(methyl acrylate) themselves had no effect on the thermal stability of PVC, but the addition of P(DBTM-St-MA) improved thermal stability of PVC. The possible reasons that thermal stability of P(DOTM-St-MA) was better than others stabilizers mentioned earlier.This can be explained as follows:

a. St and methyl acrylate chain segments in terpolymer had good compatibility with PVC because solubility parameters of polystyrene

a. color changes of samples with time
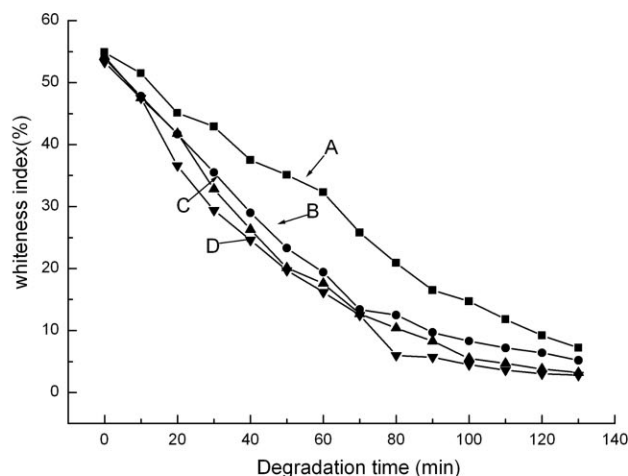
b. whiteness index changes of samples with time
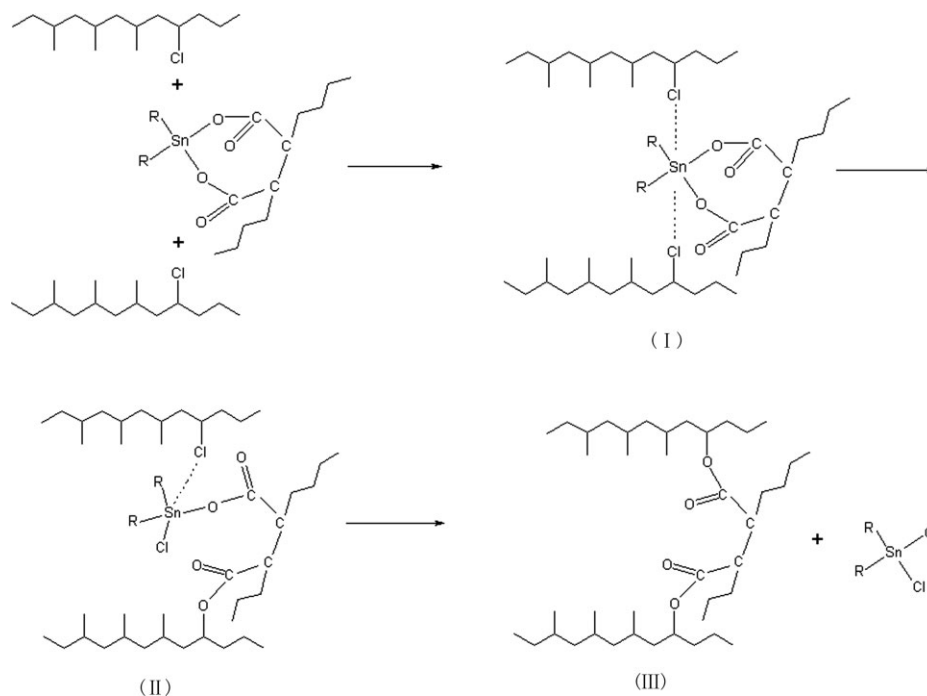
Figure 5 Thermal ageing of PVC.

Figure 6 Interaction of chain segments between PVC and polymeric organotin.

(δ = 16.2–16.6) and poly(methyl acrylate)(δ = 20.1–20.7) were near to that of PVC (δ = 19.4–20.5). Therefore, P(DOTM-St-MA) and P(DBTM-St-MA) were easier to be dispersed than low-molecular weight organic tin in compounding process. The molecular interaction between PVC and polymeric stabilizer significantly improved the thermal stability of PVC, but low-molecular organic tin had poor compatibility with PVC and tended to agglomerate during the process. The irregular distribution caused the decreasing of its thermal stability.

b. The compatibility of octyl group (octane δ = 15.4) with PVC was better than that of butyl group (butane δ < 14.4), which also induced the compatibility of P(DOTM-St-MA) with PVC was better than that of P(DBTM-St-MA).

c. Low-molecular weight stabilizers had higher thermal weight loss than polymeric stabilizers in the process of handling sample. Furthermore, the thermal stabilizing mechanism of polymeric stabilizer might be different from that of low-molecular weight organotin.

Thermal stabilizing mechanism of polymeric organotin

There were no studies on stabilizing mechanism of polymeric organotin reported in literatures, and so primary study was carried out to explain the mechanism. During PVC processing, Sn atom of polymeric

organotin could build coordinate bond with chlorine atom of PVC, which further forms comoles compound (I, Fig. 6). In the comoles compound, maleate radical of polymeric organotin replaced reactive chloride of PVC step by step and then form ester bonds[28] (II and III, Fig. 6), which stops further degradation of PVC. Moreover, molecular chains of PVC and polymeric organotin developed the same orientation (Fig. 7) in PVC processing, which improves the collision probability between tin and chlorine of PVC.
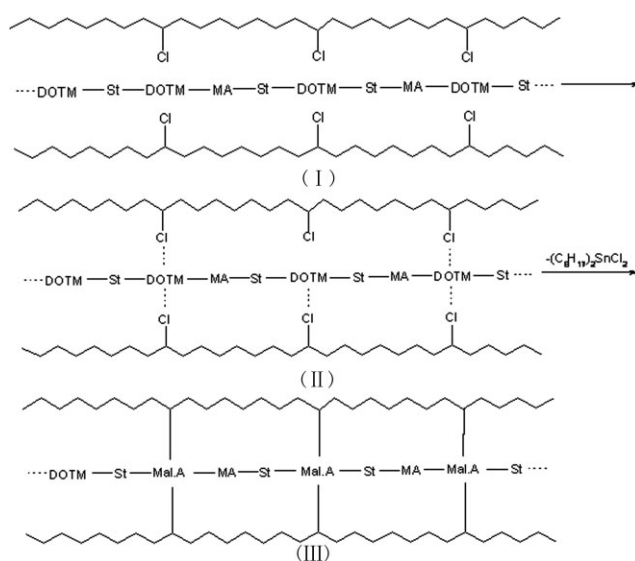

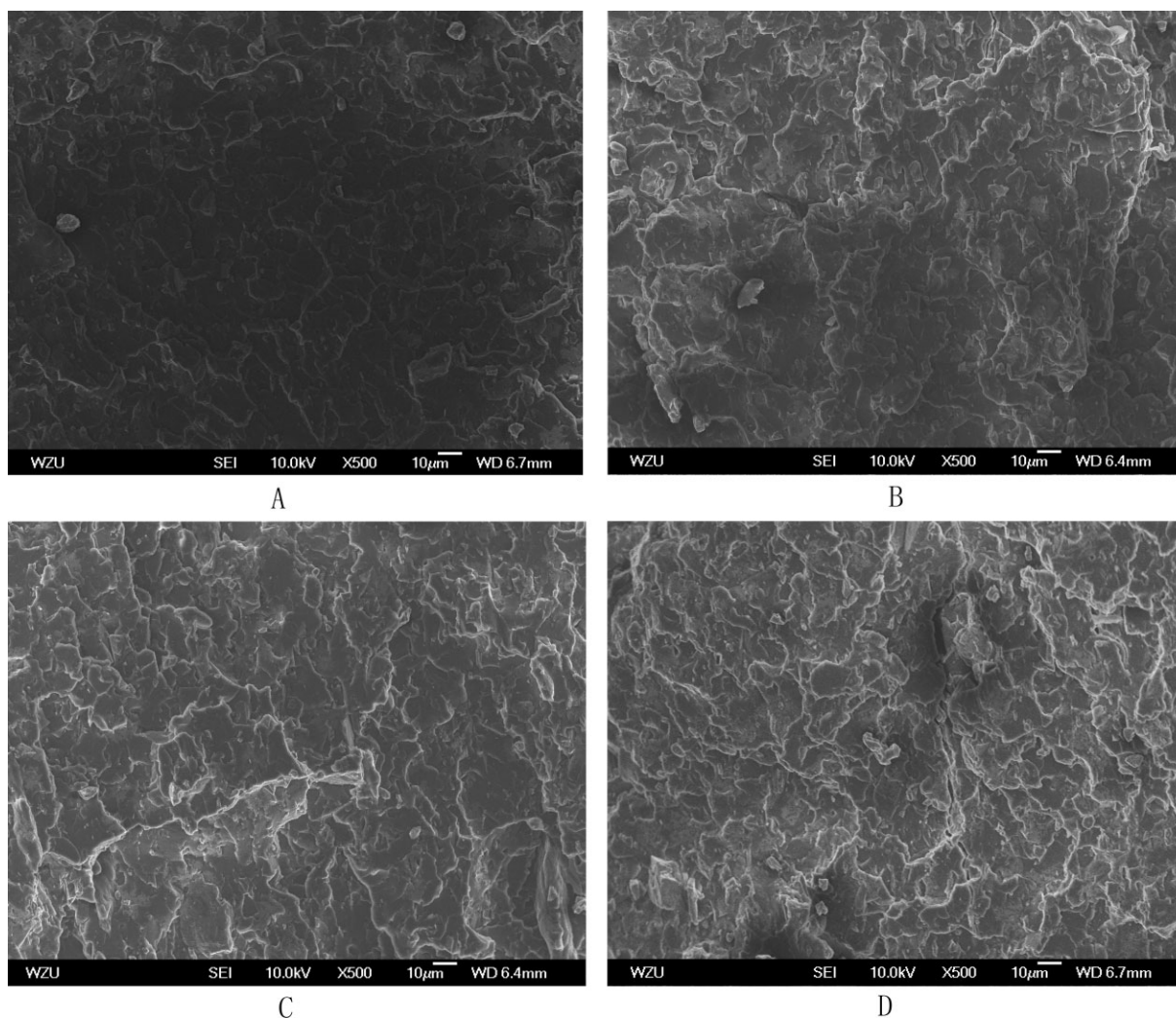**Figure 7** Interaction of intermolecules of polymeric organotin and PVC.

Figure 8   SEM images of samples.

SEM images (Fig. 8) showed the fracture surface morphology of four samples. The samples B, C, and D have a clear two-phase interface, and the particles of the dispersion phase are bigger. However, the two-phase interface of sample A is fuzzy, and the particles of the dispersion phase are smaller. This also indicated that P(DOTM-St-MA) had the best compatibility with PVC compared with the other three stabilizers. Therefore, good compatibility with PVC and low-thermal degradation ensured that P(DOTM-St-MA) was a high efficiency stabilizer for PVC.

CONCLUSIONS

Radical solution polymerization technique was used to synthesize a novel polymeric thermal stabilizer P(DBTM-St-MA), which had a higher molecular weight and narrower distribution. The terpolymer structure was confirmed by the spectra of FTIR and ^{1}H-NMR. Intrinsic thermal stability of P(DOTM-St-MA) was superior to that of P(DBTM-St-MA) and

low-molecular weight organotin. Also, the former had better compatibility with PVC, which is an important applied value in PVC processing. The evaluations of stability of the four compounds for PVC, restraining dehydrochlorination and resisting thermal ageing, were carried out, and the results show that thermal stability sequence was P(DOTM-St-MA) > P(DBTM-St-MA) > DOTM > DBTM. Therefore, P(DOTM-St-MA) is a very promising polymeric stabilizer for PVC processing.

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