

Blends of High Density Polyethylene with Branched Poly(styrene-*co*-dodecyl acrylate): Rheological, Mechanical, and Thermal Properties

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ABSTRACT: Branched poly(styrene-*co*-dodecyl acrylate) (BPSDA) was prepared by the atom transfer radical copolymerization of styrene with dodecyl acrylate using *p*-cholomethyl styrene as initiator-monomer (inimer) and CuCl/Bpy (2,2'-bipyridine) complex as catalyst. The remarkable discrepancies between the molecular weight determined by gel permeation chromatography and multiangle laser light scattering reveals the highly branched structure of the resulting copolymer. Furthermore, the composition was analyzed by hydrogen nuclear magnetic resonance (¹H NMR), which is consistent with the feed ratio of monomers. Blending of the branched product with high density polyethylene (HDPE) was attempted in haake mixer. The rheological, mechanical, and thermal stability properties of the resulting blends were studied. Compared

with pure HDPE, the complex viscosity of blend with addition of 4 wt % BPSDA decreased by 15.9%. While the elongation at break decreased by 5.5% and tensile strength decreased by 4.2%. SEM (scanning electron microscopy) revealed that the average particle size of disperse phase in HDPE/4% BPSDA blend is 0.45 μm in diameter. Differential scanning calorimetry characterization showed that the addition of BPSDA accelerated the relative crystallization rate but decreased the final absolute degree of crystallinity. No obvious change of thermal stability of the blends was observed relative to pure HDPE. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1618–1624, 2008

Key words: branched polymers; self-condensing vinyl polymerization; blend; high density polyethylene; melt modifier

INTRODUCTION

Hyperbranched polymers are a new class of three-dimensional (3D) molecules prepared by special synthetic routes that incorporates repetitive branching sequences to create an unusual architecture. Because of the compact, 3D structure of hyperbranched polymers, these molecules mimic the hydrodynamic volume of spheres in solution or in the melt. These results in a low melt viscosity, even at high molecular weights, due to a lack of restrictive interchain entanglements. This property of hyperbranched polymers make them excellent candidates for additives that could act as melt modifiers of plastics.¹ In 1995, Kim and Webster² first reported that the addition of a small amount of hyperbranched poly(phenylene) could decrease the melt viscosity of polystyrene,

obviously with a concomitant sacrifice in the maximum tensile strength. Schmaljohann et al.³ studied the blends of hyperbranched polyesters modified with dodecanoyl chloride and different polyolefins and found that the complex melt viscosity of the blends was lower than that predicted by the additive effect of the linear mixing rule with little change in the dynamic mechanical behavior. Massa et al.⁴ studied the phase behavior and mechanical properties of blends of both hydroxy-terminated and acetate-terminated all-aromatic hyperbranched polyesters with a variety of linear polymers. They found that the blends showed increased tensile and compressive moduli but decreased elongation at break and toughness compared to unmodified PC. Hong et al.⁵ investigated the use of a dendritic additive from Sweden Perstorp Specialty Chemicals as a processing aid for linear low-density polyethylene in a tubular film blowing process. Through the addition of one dendritic additive, "sharkskin" was successfully eliminated and the processing rate was enhanced. Mulhern and Tan⁶ studied a series of blends of hyperbranched polyesters terminated by hydroxyl group with high molecular weight polystyrenes and found that a significant drop in the blends viscosity

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occurs immediately on addition of hyperbranched polyesters. Jang et al.⁷ investigated the effect of terminal groups, including hydroxyl, acetate, and benzoate, on the crystallization and rheological properties of the blends of poly(ethylene terephthalate) with hyperbranched aliphatic polyesters. These results showed that hyperbranched aliphatic polyesters can act as rheological modifiers in the blends and the blends with addition of 20 wt % hyperbranched polyesters with acetate terminal groups has the lowest complex viscosity but the mechanical property was not discussed. Qin et al.⁸ used allyl-functionalized hyperbranched polyimide as modifier of bisphenol-A based bismaleimide resin (BPSDAA-BMI) and found that blends containing 4 wt % AT-PAEKI has a dramatic (65-fold) reduction in the viscosity and the cured modulus was increased by approximately 10%.

It can be noted that all the hyperbranched polymers employed in the aforementioned examples are prepared from condensation method proposed by Flory⁹ in 1952 and most of them are hyperbranched polyesters. Since Fréchet et al. first reported the synthesis of hyperbranched polymers by self-condensing vinyl polymerization (SCVP) in 1995,¹⁰ the species of hyperbranched polymers have been extended greatly and hyperbranched polymers based on styrene and its derivatives,^{11–13} acrylates and methacrylates,^{14–17} maleimide,^{18–19} and isobutylene²⁰ all have been prepared. Our group has reported the use of highly branched polystyrene prepared by ATRP as melt modifier for polycarbonates.²¹ In this work, we prepared a novel branched polymer from the atom transfer radical copolymerization of styrene and dodecyl acrylate using *p*-chloromethyl styrene as initiator-monomer (inimer) and then the addition of the resulting branched copolymers as melt modifier in high density polyethylene was attempted. The dodecyl segments in the copolymer were expected can provide somewhat compatibilization of polyethylene with the branched copolymer.

EXPERIMENTAL

Materials

4-(Chloromethyl) styrene (CMS, Aldrich) (New Jersey, US) was washed with 5% NaOH solution followed by distilled water three times and then dried using anhydrous Na₂SO₄ before use. Styrene, analytical reagent from Shanghai chemical reagent company, was distilled under reduced pressure. Dodecyl acrylate (DA, 99%, Shanghai chemical reagent company) was washed like CMS and then was extracted from water using ether. Ether was removed by vacuum to obtain dodecyl acrylate. 2,2'-bipyridine (Bpy, analytical reagent, Shanghai chemical reagent company) was used as received. Copper (I) chloride

(CuCl, analytical reagent, Shanghai chemical reagent company) was purified by stirring in acetic acid, washing with methanol, and then dried under reduced pressure. High density polyethylene (HDPE), 5000S form Yangzi petroleum chemical company in Nanjing, Jiangsu Province of China, was dried under reduced pressure before use.

Synthesis of branched poly(styrene-*co*-dodecyl acrylate) (BPSDA) and branched polystyrene

CMS (1.693 g, 11.1 mmol), dodecyl acrylate (13.223 g, 55.5 mmol), styrene (11.56 g, 111.1 mmol), Bpy (1.04 g, 6.66mmol), and CuCl (0.33 g, 3.33mmol) and a magnetic stirring bar were added into a dry 100 mL round bottom flask. The flask was cycled between vacuum and argon >five times to remove the oxygen. Then, the flask was sealed and placed in a preheated, thermally regulated oil bath at (110 ± 1)°C. After 24 h polymerization under stirring, the reaction mixture was dissolved in acetone and precipitated into methanol. Repeat the dissolution and precipitation twice to remove the catalyst completely. The resulting product was dried under vacuum at room temperature for 72 h to yield the branched copolymers (Yield: 75%). Branched polystyrene (BPS) was synthesized according to the similar formulation and procedure aforementioned besides that 55.5 mmol dodecyl acrylate was replaced by 55.5 mmol styrene (Yield: 80%).

Blending

The blends were mixed in small batches of approximately 50 g in the Haake Rheomix mixer driven by a Haake Rheocord 90 System, which can output the required torque on line. All of the blends were processed under the same conditions. The processing temperature for the blends was 160°C and processing speed was 50 rpm. The blends were prepared by first melting the HDPE in the mixer followed by the addition of the BPSDA or BPS. Once the BPSDA or BPS was added to the molten base polymer, the two materials were blended for several minutes until the level-off of the torque-time curve. For comparison, pure HDPE was treated in the same way as the blends.

Characterization methods

Gel permeation chromatography (GPC) was performed on a GPC line consisting of a Waters 1515 Isocratic HPLC Pump, Waters syringe HR 4e, HR 1, and HR 0.5 column, and a Waters 2414 Refractive Index Detector at room temperature. The eluent was tetrahydrofuran with a flow rate of 1 mL/min and the data were obtained with linear polystyrene standards. Multiangle laser light scattering (MALLS) was

conducted on 703-T mini DAWN Tristar Light Scattering Photometer. The dn/dc values of the resulting copolymer was determined using an Optilab rEX ($\lambda = 690$ nm) interferometric refractometer (Wyatt) in off-line mode at 25°C. The dn/dc values of BPSDA and BPS were calculated to be (0.1323 ± 0.0024) mL/g and (0.184 ± 0.0018) mL/g, respectively. The weight-average molecular weights of the branched copolymers were calculated using the calculated dn/dc values. The nuclear magnetic resonance (NMR) spectroscopy were taken on a Bruker ARX-300 type NMR spectrometer at room temperature in $CDCl_3$. Thermal gravimetry analysis (TG) and derivative thermal gravimetry (DTG) were carried out on SDTQ-600 thermalgravimetric analyzer under N_2 atmosphere in the temperature range of 50–650°C, at a heating rate of 20°C/min. Postprocessing rheological studies were carried out according to ASTM Standard D4440-95. Modular Compact Rheometer (MCR) of Anton Paar Company was used in a frequency sweep mode over a range of 0.01–100 s^{-1} . Tensile properties measurement was performed according to ASTM D 638-90. Five specimens were tested for each sample. Morphology was evaluated using scanning electron microscopy. Samples were prepared by freezing the polymer blends in liquid nitrogen followed by high-speed impact to create fresh fracture surfaces. To improve contrast for image analysis, the dispersed phase was removed by submerging the samples in acetone for 4 h, a selective solvent for the BPSDA and BPS. Then fracture surfaces were covered with a layer of gold and examined with a JEOL JSM-6030LA Scanning Electron Microscope. Image analysis techniques were employed to determine the average particle size and size distribution of disperse phase. Nonisothermal crystallization process analysis was performed on a Perkin-Elmer DSC-7 under N_2 atmosphere. The sample was heated to 190°C at a heating rate of 50°C/min, kept for 10 min, and quenched to 50°C at a cooling rate of 10°C/min. The corresponding crystallization exotherm was obtained as a function of temperature. The absolute degree of crystallinity (X_C) of the PE phase was determined from the ratio of heat of fusion (ΔH_m) of PE phase to the heat of fusion of 100% crystalline phase (ΔH_{m0}). ΔH_{m0} is set as 271.74 J/g.²²

RESULTS AND DISCUSSION

Characterization of the copolymer

p-Cholomethyl styrene (CMS) is one of the widely used and commercially available inimer to prepare branched polymer via self-condensing vinyl copolymerization.^{11,12,18} Because of the remarkable reactivity discrepancy of primary benzylic chloride ($-PhCH_2Cl-$) and secondary benzylic chloride

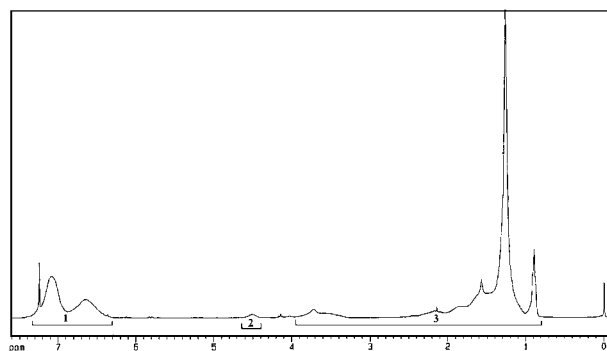


Figure 1 1H NMR spectrum of branched poly(styrene-co-dodecyl acrylate).

($-PhCHCl-$) to initiate atom transfer radical polymerization (ATRP), a higher ratio of catalyst to inimer favors the formation of branched structure.¹² The mole ratio of $CuCl$ to CMS employed in this work is 0.3 and the 1H NMR spectrum of the resulting copolymer is shown in Figure 1. According to the classical SCVP mechanism,¹⁰ each polymer chain in our work should have one double bond and a number of chlorine atoms. The first set of signals, at 6.3 ~ 7.2 ppm, arises from the aromatic protons, which is assigned as region 1. The signals from methylene and methine proton of the remaining double bond at 5.2, 5.7, and 6.6 ppm are almost invisible. The signal with chemical shift of 4.5 ppm is due to the methine protons adjacent to the chlorine atoms, which is assigned as region 2. The peaks with chemical shift of 3.3 ~ 3.8 ppm derive from protons of methylenes adjacent to ester group in dodecyl acrylate segments. The signals with chemical shift of 0.89 ppm are due to the methyl protons in dodecyl acrylate segments. The signals with strongest intensity with chemical shift of 1.27 ppm are due to the protons of 10 methylenes in dodecyl acrylate segments. The broad sets of signals, from 1.4 to 2.5 ppm, are due to the methylene and methine protons in polymer chains and that in benzyls from CMS after loss of chloride atoms. The region with chemical shift lower than 4 ppm is assigned as region 3. If S_1 , S_2 , and S_3 denote the areas of region 1, 2, and 3, respectively. The area of peak due to $CHCl_3$ in region 1 has been calculated by comparing the height of this peak with that of the peak attached to inner standard TMS (tetramethylsilane) and has been deducted from S_1 . The number of structure unit of dodecyl acrylate (DA), N_{DA} , and that of CMS and Styrene, N_{St} , can be related by the eq. (1) approximately, regardless the small discrepancy of the number of aromatic protons in styrene and CMS unit structure.

$$\frac{3N_{St} + 28N_{DA}}{S_3 - S_2} = \frac{5N_{St}}{S_1} \quad (1)$$

TABLE I
The Characteristics of the Resulting Branched Poly(styrene-co-dodecyl acrylate) (BPSDA) and Polystyrene (BPS)

Feed ratio	$\overline{M}_{n,GPC} \times 10^{-4}$	$\overline{M}_{w,GPC} \times 10^{-4}$	$\frac{\overline{M}_{w,GPC}}{\overline{M}_{n,GPC}}$	$\overline{M}_{w,MALLS} \times 10^{-4}$	$\frac{\overline{M}_{w,MALLS}}{\overline{M}_{w,GPC}}$
1 : 5 : 10 : 0.3 : 0.6 ^a	3.4	9.4	2.76	13	1.38
1 : 15 : 0.3 : 0.6 ^b	2.9	8.5	2.93	12	1.41

^a The feed ratio is expressed as [CMS] : [DA] : [styrene] : [CuBr] : [Bpy].

^b The feed ratio is expressed as [CMS] : [styrene] : [CuBr] : [Bpy].

$$\overline{F}_{DA} = \frac{N_{DA}}{N_{DA} + N_{St}} \quad (2)$$

Based on the eq. 1, the mole fraction of DA structure unit in the resulting copolymers, \overline{F}_{DA} can be calculated according eq. 2. The mole feed ratio of CMS, DA, and styrene is 1 : 5 : 10 and \overline{F}_{DA} is 30% calculated from above equations, which is nearly consistent with the DA mole fraction of 31.25% in the monomer composition. The characteristics of the resulting BPSDA and BPS synthesized for control experiment are shown in Table I.

The smaller hydrodynamic volume of highly branched polymer will lead to longer retention time in GPC, the molecular weight of hyperbranched polymer obtained by GPC, which is apparent value based on linear polystyrene standards, is lower than that determined by other methods, such as ¹H-NMR and MALLS.¹¹ The significant discrepancy observed in the M_w determined by GPC and MALLS in Table I indicates the highly branched structure of the copolymer prepared in this work.

Rheological behavior and morphology of polymer blends

The blending was conducted in a low capacity Haake mixer. Figure 2 and Table II show the torques

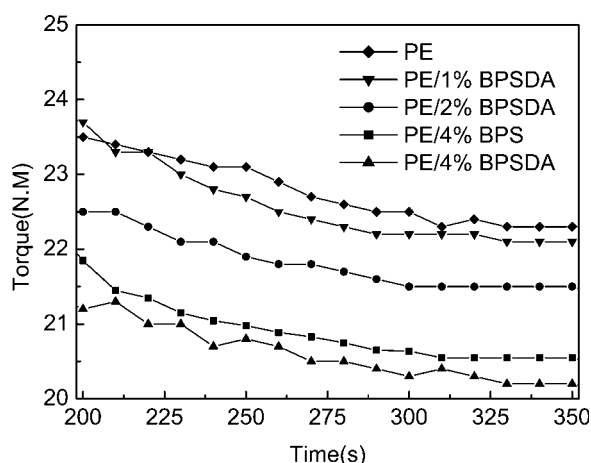


Figure 2 Required torque of HDPE with addition of various content of BPSDA or BPS during mixing.

required in processing of blends with various BPSDA or BPS content and pure HDPE. It was observed that with as little as 1 wt % BPSDA added, the torque in the mixer dropped to certain extent relative to that required to process the pure HDPE under the same conditions. Addition of 2 wt % and 4 wt % BPSDA made the required torque much lower, which decreased by 3.2% and 8.6%, respectively, relative to that of pure HDPE. Furthermore, the rheological behavior of the blends and pure HDPE were studied by using physical Modular Compact Rheometer and the results are shown in Figure 3 and Table II. The complex viscosity decreased with the increase of content of BPSDA in the blends. When the shear rate is 100 s⁻¹, the complex viscosity of blends with addition of 2 wt % and 4 wt % BPSDA decreases by 7.6% and 15.9%, respectively, relative to that of pure HDPE. This indicates a significant enhancement in the processability of the blend due to the addition of BPSDA. The highly branched BPSDA macromolecules act as intermolecular lubricant. Compared with BPSDA, addition of 4% BPS of nearly equivalent molecular weight in HDPE also can results in a decreased torque and complex viscosity (Figs. 2, 3, and Table II). But it can be observed that the lubricating effect of BPS is less than BPSDA. The morphology observed from the fracture surfaces of the HDPE/4% BPS and HDPE/4% BPSDA are shown in Figure 4. The average particle size of disperse phase in the HDPE/4% BPS

TABLE II
Rheological Parameters of Pure HDPE and Blends with Various Content of Branched Polymers

Sample	Branched polymer/ HDPE (wt %)	Torque (N m) ^a	Complex viscosity at shear rate of 100 s ⁻¹ (Pa s) ^b
1	0	22.1	1983
2 ^c	1.0	21.8	1905
3 ^c	2.0	21.4	1832
4 ^c	4.0	20.2	1668
5 ^d	4.0	20.6	1804

^a The stable torque of the final stage in Figure 2.

^b The complex viscosity obtained from Figure 3.

^c The branched polymer is BPSDA.

^d The branched polymer is BPS.

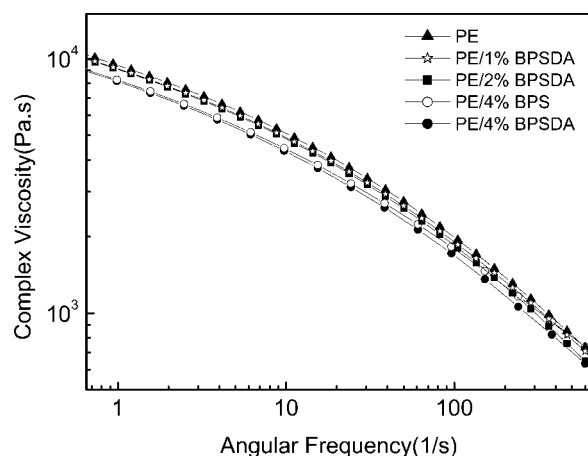


Figure 3 Rheological behavior of HDPE with the addition of BPSDA or BPS.

blend is 1.52 μm in diameter with standard deviation 0.57 μm (Table III). The morphology of the HDPE/4% BPSDA exhibits an average particle size of 0.45 μm in diameter with standard deviation 0.22 μm . The

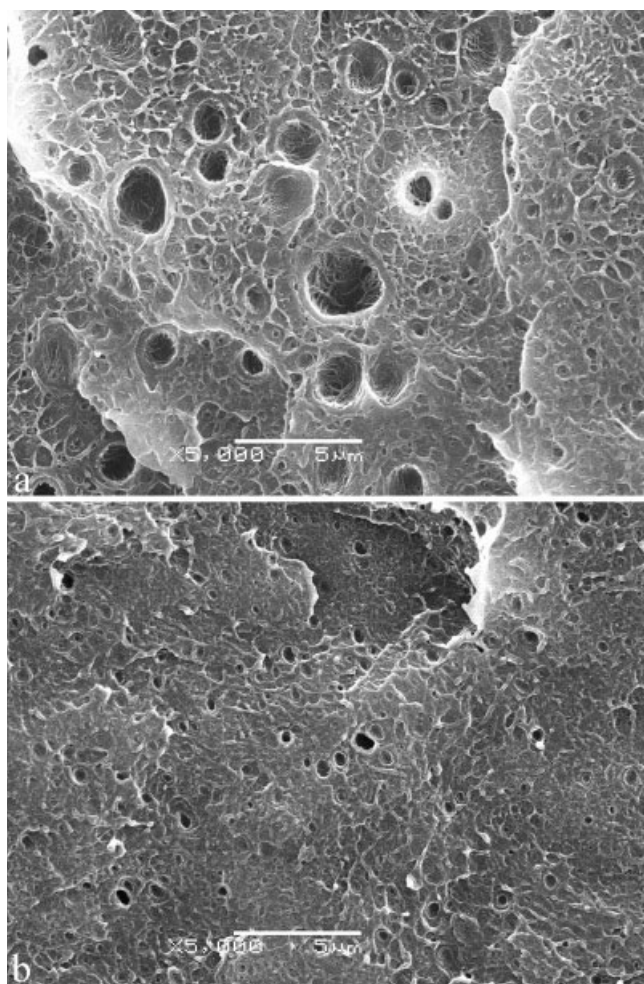


Figure 4 SEM micrographs of blends of (a) HDPE/4% BPS; (b) HDPE/4% BPSDA.

TABLE III
Disperse Phase Particle Size Distribution of Two Blends

	HDPE/ 4% BPS	HDPE/ 4% BPSDA
Average diameter ($\text{m} \times 10^{-6}$)	1.52	0.45
Standard deviation ($\text{m} \times 10^{-6}$)	0.57	0.22

observed decrease in particle size in the BPSDA blend may be attributed to a reduction of the interfacial tension resulting from the compatibility of dodecyl segments with HDPE. Generally, the remarkable compatibility of hyperbranched processing aids with matrix polymer resulting from the formation of copolymer compatibilizers can greatly reduce the lubricating effect.⁶ While, in our case, there is no chemical reaction between the branched polymers and matrix polymer. The worse dispersion of BPS relative to HPSDA in HDPE made BPS macromolecules can not act as intermolecular lubricant sufficiently.

Mechanical and crystallization property

As shown in Table IV, the tensile strength and elongation at break of the blends decrease relative to that of pure HDPE. The more BPSDA is added, the higher dropping extent can be observed. When 4 wt % BPSDA was added, the elongation at break decreased by 5.5% and tensile strength decreased by 4.2%. The decrease of tensile strength and elongation at break of HDPE/4% BPS blend relative to pure HDPE is more remarkable, which results from the poor compatibility of BPS with HDPE (Fig. 4). On the other hand, it is regarded that the crystallinity behavior of HDPE has remarkable influence on its property. The melting and crystallization parameters of HDPE/BPSDA blends determined from DSC are shown in Table V. T_m , melting point, is defined as the peak temperature of melting endotherm. T_p is the peak temperature of crystallization exotherm. n is avrami constant obtained based on avrami equation. $t_{1/2}$ is the half-time of crystallization, which

TABLE IV
Tensile Properties of HDPE and Blends with Various Content of Branched Polymers

Sample	Branched polymer/ HDPE (wt %)	Tensile strength (MPa)	Elongation at break (%)
1	0	28.5 \pm 4.8	1040 \pm 64
2 ^a	1.0	28.3 \pm 4.5	1020 \pm 70
3 ^a	2.0	27.5 \pm 5.0	997 \pm 68
4 ^a	4.0	27.3 \pm 5.1	982 \pm 73
5 ^b	4.0	25.4 \pm 5.4	934 \pm 84

^a The branched polymer is BPSDA.

^b The branched polymer is BPS.

TABLE V
Melting and Crystallization Parameters of HDPE and HDPE/BPSDA Blends

Content of BPSDA (wt %)	Melting parameters			Crystallization parameters		
	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_p (°C)	$t_{1/2}$ (s)	n
0	133.11	194.02	71.4	117.64	19.92	2.8
1.0	132.94	193.38	71.2	117.34	17.82	2.6
2.0	132.73	187.81	69.1	117.52	16.62	2.3
4.0	130.56	172.42	63.5	117.46	15.30	2.4

means the relative degree of crystallinity is 50%. All the aforementioned parameters of pure HDPE and HDPE phase in HDPE/BPSDA blends can be obtained from the melting endotherms and crystallization exotherms of the corresponding samples.^{23,24} As the content of BPSDA in the blends is increased, the T_m , X_c , and $t_{1/2}$ are decreased. The avrami constant for pure HDPE is near to 3, while that of blends with 2 and 4% BPSDA are near to 2. It seems that a small amount of BPSDA can play the role of a nucleating agent during the crystallization of HDPE in HDPE/BPSDA blends. The facility of nucleation results in high crystallization rate of HDPE. While the presence of BPSDA phase also results in the decrease of chain diffusion of HDPE and so has a reverse effect to the absolute degree of crystallinity. Jang et al.⁷ also revealed that the addition of a small amount of hyperbranched polyester in poly(ethylene terephthalate) could greatly reduce the degree of crystallinity of PET. The loss of tensile property of HDPE/BPSDA blends may result from the poor mechanical property of highly branched polymer itself and somewhat reduced absolute degree of crystallinity of HDPE in the blends. While as mentioned earlier, the complex viscosity corresponding to the

same sample decreased by 15.9%. So the sacrifice of mechanical property may be acceptable.

Thermal stability

Generally, the hyperbranched polymers prepared from ATRP have lower thermal stability due to the presence of many labile carbon halide terminal groups.¹² When hyperbranched polymers prepared from ATRP are blended with linear polymers, its effect on the thermal stability of the prepared blends is needed to be investigated. The thermal gravimetry analysis results are shown in Figure 5 and Table VI. All the blends have initial weight loss temperatures higher than 466°C and statistic heat-resistant index T_s higher than 224°C. Even the cleavages of labile carbon halide bonds in BPSDA produce some radicals, HDPE macromolecules are not easily be attacked to undergo degradation since there is no labile sites like tertiary hydrogen atoms in the chain of HDPE macromolecules. So the addition of small amount of BPSDA does not deteriorate the thermal stability of HDPE blends.

CONCLUSIONS

Branched poly(styrene-*co*-dodecyl acrylate) (BPSDA) was prepared by atom transfer radical copolymerization of *p*-cholomethyl styrene, styrene, and dodecyl acrylate with the mole feed ratio of 1 : 10 : 5. The

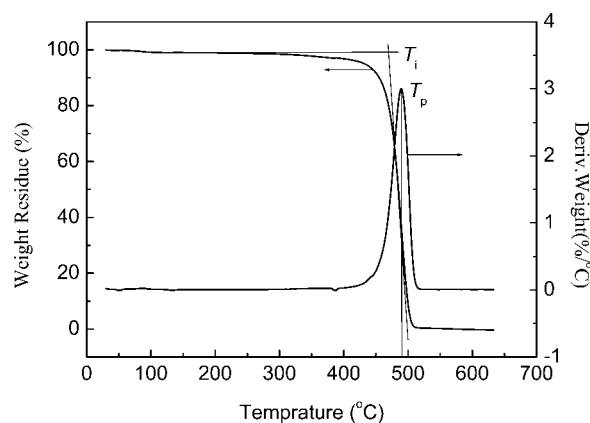


Figure 5 TG and DTG thermograms of blends with 4 wt % addition of BPSDA. Initial weight loss temperature T_i is the temperature corresponding to the point of intersection of the baseline and the tangent at T_p . T_p is the temperature with the fastest weight-losing rate determined by DTG.

TABLE VI
TG Results of Pure HDPE and Blends with Various Content of BPSDA

Content of BPSDA (wt %)	T_i^a (°C)	T_5^b (°C)	T_{30}^b (°C)	T_s^b (°C)
0	469.5	431.8	475.4	224.4
1.0	466.5	442.2	474.2	226.0
2.0	466.8	433.0	473.5	224.0
4.0	470.3	439.2	479.4	227.0

^a Initial weight loss temperature from extrapolation methods as shown in Figure 5.

^b T_5 , T_{30} : Temperature of 5% and 30% weight loss; $T_s = 0.49[T_5 + 0.6(T_{30} - T_5)]$.

weight average molecular weight of the resulting polymer determined by GPC is 94,000 and that determined by MALLS is 130,000. The remarkable discrepancy between the two values reveals the highly branched structure of the resulting copolymer. The mole fraction of dodecyl acrylate structure unit in the copolymer determined by ^1H NMR is 30%. The novel blends of HDPE with BPSDA were prepared in haake mixer. Compared with pure HDPE, the complex viscosity of blend with addition of 4 wt % BPSDA decreased by 15.9%. While the elongation at break decreased by 5.5% and tensile strength decreased by 4.2%. SEM revealed that the average particle size of disperse phase in HDPE/4% BPSDA blend is 0.45 μm in diameter. DSC characterization showed that the addition of BPSDA accelerated the relative crystallization rate but decreased the final absolute degree of crystallinity. No obvious change of thermal stability of the blends was observed relative to pure HDPE.

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