Cocrystallization Behavior of Poly(*n*-Docosyl Acrylate) with *n*-Docosanoic Acid by X-Ray and Differential Scanning Calorimetry Studies

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ABSTRACT: Cocrystallization behavior of comb-like poly(*n*-docosyl acrylate) (PDA) with *n*-docosanoic acid (C_{22}) has been studied by means of differential scanning calorimetry (DSC) and X-ray diffraction (XRD) methods. The DSC curves of blended samples of neat PDA with C_{22} show the characteristic melting endotherms that correspond to the melting of the crystallites. DSC measurements of PDA/C_{22} blends also suggest the existence of another crystalline form induced by the addition of the C_{22}. From the XRD measurements, the existence of hexagonally-packed crystalline lattice and the phase behavior of PDA/C_{22} blends at different mole percent are confirmed. Thermal degradation behavior of PDA and its corresponding blends with C_{22} is studied by thermogravimetric analysis. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2140–2146, 2005

Keywords: cocrystallization; poly(*n*-docosyl acrylate); polymer blends; comb-like polymers; differential scanning calorimetry (DSC); X-ray diffraction; thermogravimetric analysis (TGA)

INTRODUCTION

A number of polymeric compounds such as homopolymers of alkyl acrylates and methacrylates and their copolymers with ethylene, vinyl acetate, etc., are extensively used as pour point depressants /flow improvers, viscosity index improvers in high waxy crude oils, lubricating oils, and fuel oils. These additives can reduce the growth of wax crystal structure, either by cocrystallization or by absorption forming smaller crystals of higher volume to surface ratio,[1,2] thus preventing gelation.[3] Due to a change in crystalline shape, the ability of the wax crystals to intergrow and interlock is greatly diminished, thus resulting in considerable lowering of the pour point. Poly(*n*-docosyl acrylate) (PDA) may be considered a typical short branched comb-like polymer because each has one long alkyl side chain on every two main chain carbon atoms. These comb-like polymers absorb strongly to the main growth faces of the wax crystal and do so in a manner that breaks down the characteristic lamella structure found in wax crystal.[4] These polymers crystallize through alkyl side chain packing, independently of the stereoregularity of the main chain.

Comb-like polymers, which have crystallizable long alkyl side chains being attached to the amorphous main chain, are known to pack into a layered structure with alternating crystalline side chain region and amorphous main chain region in the solid state.[5] An X-ray diffraction profile of such polymers has an intense reflection corresponding to the Bragg spacing *d* of 4.16 Å, which suggests the formation of hexagonal crystalline *n*-alkyl side chain.[6] There also exists a shoulder in the smaller angle region that is considered to originate from the layered structure. *n*-Alkyl side chains in comb-like polymers are able to crystallize when they reached a minimum length, and generally they crystallize in hexagonal structure. Plate et al.[7] proposed a two-layer structure for PDA and a one-layered structure for poly(*n*-docosyl methacrylate) (PDMA) to establish the diffraction pattern of PDA and PDMA, respectively. Disordered packing of the end groups of the side chains occur and the polymer chains are arranged with the shift toward the extended side chains axis, which leads to smaller value of layer spacing for the one-layer model of PDMA.[7] While in the two-layer model of PDA, the side chains extended on both sides of the main chain. Later, Hsieh et al.[8] reported that the intercalating side chains pointing in opposite directions form the crystalline layer. Although detailed solid-state structure of comb-like polymers has not been established, the layered struc-
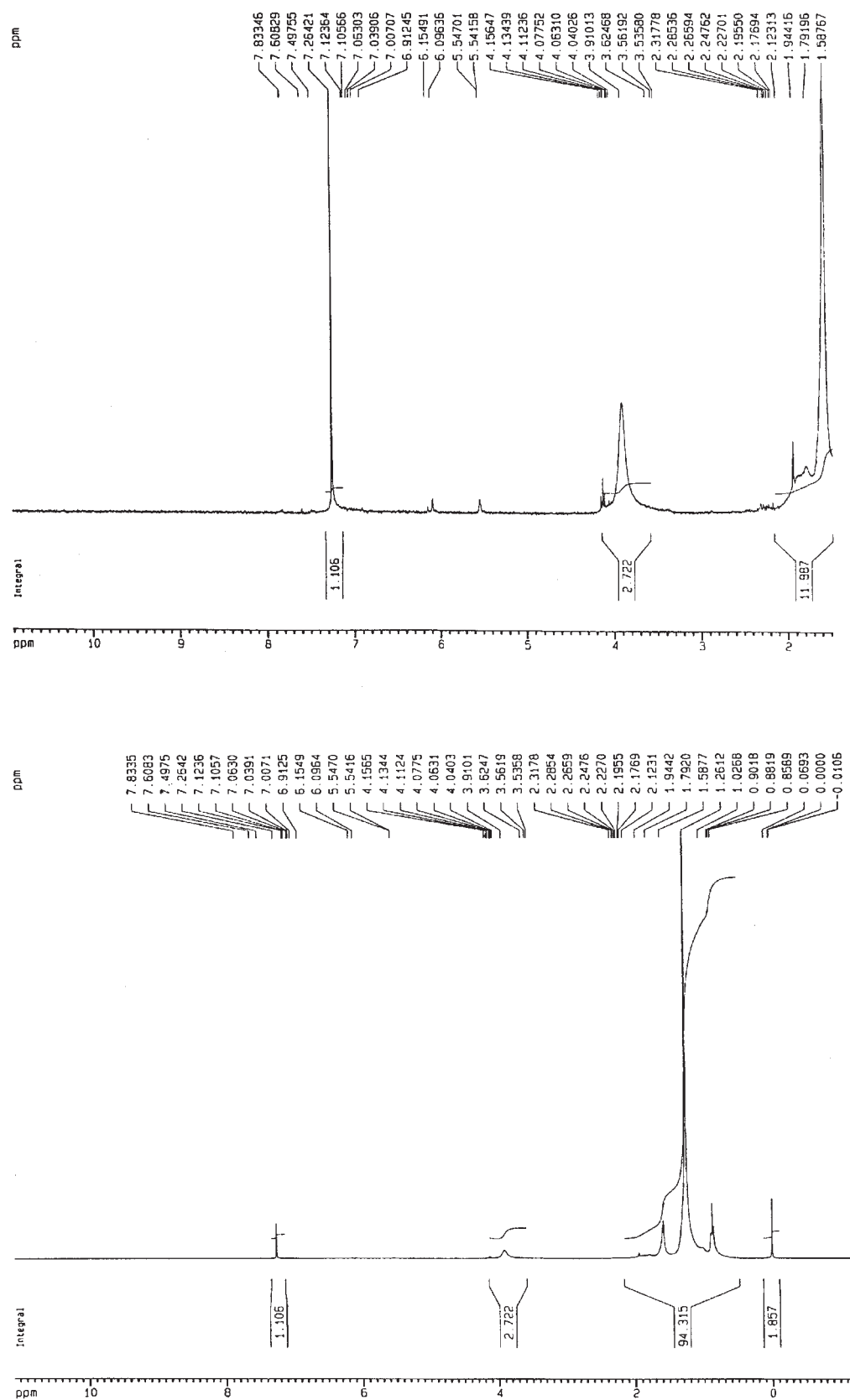
Figure 1 ^{1}H-NMR of PDA synthesized by ATRP of *n*-docosyl acrylate (DA) at 80°C in the presence of AIBN as the source of reducing agent. Conditions: [DA] = 1.00 mol L^{-1}; [AIBN] = 1.00 × 10^{-2} mol L^{-1}; [CBr$_4$] = 1.00 × 10^{-1}; [Fe(III)] = 1.00 × 10^{-3} mol L^{-1}; [bpy] = 3.00 × 10^{-3} mol L^{-1}.
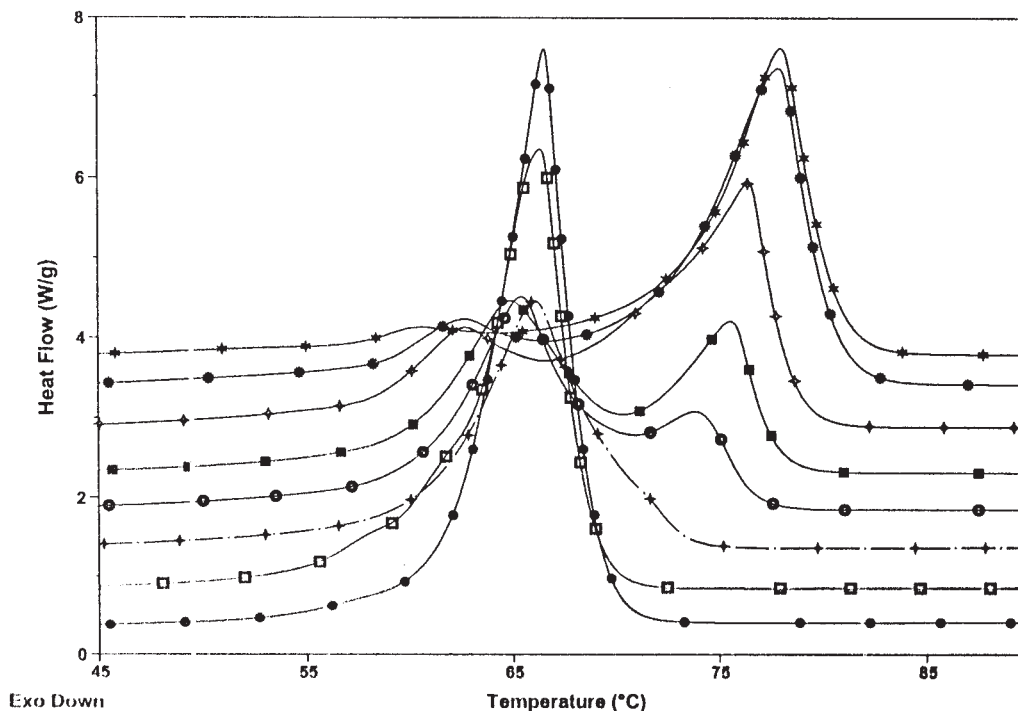
Figure 2 DSC curves for PDA blends with C_{22}, recorded in nitrogen atmosphere at a heating rate of $10°C$ min^{-1}. Mole percent of $[PDA]/[C_{22}]$ = (●) 100/0; (□) 90/10; (+) 75/25; (○) 60/40; (■) 50/50; (◇) 30/70; (●) 20/80; (*) 10/90.

ture with alternating segregation of the side chain and main chain domain is commonly accepted.[9–12] The morphology of polymer blends is complicated and depends not only on sample composition but also on the crystallization conditions.

In this study, we report the cocrystallization behavior of PDA with C_{22} by differential scanning calorimetry (DSC) and X-ray diffraction methods. The *n*-alkyl fatty acid C_{22} has a chemical structure similar to that of the side chain of the polymer and crystallizes at a temperature higher than the crystallization temperature of PDA. For blended samples, DSC measurements suggest the existence of another crystalline form induced by the addition of C_{22}. This paper also reports the thermal stability and degradation kinetics of PDA and its blends with corresponding fatty acids.

EXPERIMENTAL

PDA with low polydispersity was prepared by atom transfer radical polymerization (ATRP) as described.[13] The polymer was further purified by repeated precipitation in tetrahydrofuran/acetone system followed drying *in vacuo* overnight. The number average molecular weight (M_n) of the sample was 37,100 with a polydispersity index of 1.84. *n*-Docosanoic acid (C_{22}, BDH) and tetrahydrofuran (Qualigens) were purified by standard methods.

The blending samples of PDA with C_{22} were prepared as follows: The weighted polymer and C_{22} were

dissolved in THF casted on a glass sheet, heated at 80°C, quenched to room temperature, and dried in a vacuum. Blended samples were grounded to a fine powder to prepare homogeneously mixed samples. The compositions of the blends are expressed by the mole fraction of the monomeric units of polymer and C_{22}. Molecular weights (MW) and molecular weight distribution (MWD) of the polymers were determined using a Waters 515 gel permeation chromatograph equipped with three Styragel columns (HR1, HR3, and HR4) in series with a 2410 differential refractometer as the detector. Analysis was performed at room temper-
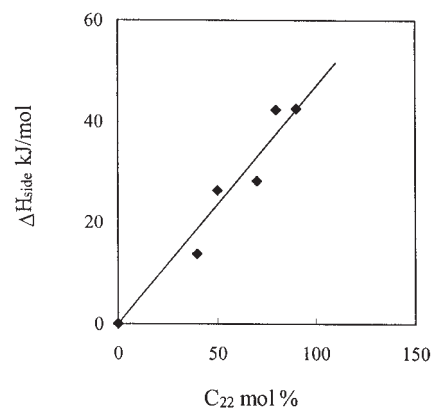

Figure 3 Plot of heat of crystallization per mole of *n*-docosyl side chain, ΔH_{side} versus C_{22} content in blends of PDA/C_{22}.

TABLE 1
Differential Scanning Calorimetric Studies of Poly(*n*-Docosyl Acrylate) (PDA) Blended with *n*-Docosanoic Acid (C$_{22}$)

Sample No.	PDA (mol %)	C$_{22}$ (mol %)	First transition			Second transition		
			Peak value (°C)	ΔH_m (kJ mol^{-1})	ΔS_m (J K^{-1} mol^{-1})	Peak value (°C)	ΔH_m (kJ mol^{-1})	ΔS_m (J K^{-1} mol^{-1})
1	100	0	66.6	71.22	209.72	—	—	—
2	90	10	66.4	63.21	186.24	—	—	—
3	75	25	66.1	46.42	136.86	—	—	—
4	60	40	65.3	24.13	71.33	74.5	13.77	39.62
5	50	50	64.7	22.04	65.27	75.7	26.42	75.79
6	30	70	62.3	21.4	63.89	76.8	28.25	80.77
7	20	80	62.2	21.4	63.12	78.0	42.20	120.5
8	10	90	60.1	1.56	4.68	78.13	42.39	120.68

ature using tetrahydrofuran (HPLC grade) as eluent at 1 mL min^{-1}. DSC curves were recorded using a TA Series DSC 2010 instrument in nitrogen atmosphere at a heating rate of 10°C min^{-1}. The instrument was calibrated with indium for correction of heat of transition. Thermal stability studies were performed using a TA Series STD 2960 simultaneous DTA-TGA analyzer in nitrogen atmosphere at a heating rate of 10°C min^{-1}. The X-ray diffractogram of polymers was recorded on a Model JDX-11P3A JEOL diffractometer with a solid sample using Ni-filtered Cu-Kα radiation at 35 kV and 10 mA in the wide angle range 2° < θ < 60°. The ^{1}H-NMR spectrum was recorded on a Bruker 300-MHz spectrometer in CDCl$_3$ with tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

Thermal analysis of polymers is very important in understanding molecular architecture, decomposition mechanism, thermal stability, etc., which help in determining utility of polymers under various environmental conditions and at high temperature applications. The crystallization behavior of polymethacrylates with long alkyl side chains has been extensively studied.[14–16] The kinetics of polymer crystallization can be studied by a number of techniques such as dilatometry,[17] polarized light microscopy,[18] and DSC.[19] In a recent report the conformational and crystallization behavior of poly(*n*-octadecyl methacrylate) was reported by SAXS and dielectrical spectroscopy.[20] Kunisada et al.[21] reported the dependence of thermodynamic parameters on the alkyl chain length from DSC studies.

The ^{1}H-NMR analysis of reprecipitated PDA is shown in Figure 1 where the important resonance has been assigned. The polymer was prepared by ATRP technique at 80°C using 2,2'-azobisisobutyronitrile (AIBN) as the radical source, CBr$_4$ as the initiator, and in the presence of FeCl$_3$/2,2'-bipyridine catalyst system. Characteristic signals for α-halocarbonyl moieties are visible at both 4.1 and 3.91 ppm. The signal at 4.1

ppm corresponds to the methylene proton in α-position of the repeated docosyl ester group and the ester group adjacent to the terminal halogen resonates at 3.91 ppm. For PMMA prepared from ethyl 2-bromopropionate, characteristic resonance originating from α-halocarbonyl moieties was observed at both 4.1 and 3.8 ppm.[22] Zhu and Yan[22] assigned the former signal to methylene protons of the ethyl ester group while the latter was assigned the methyl ester group adjacent to the terminal halogen. Similar spectra of PMMA obtained from the reverse ATRP of methyl methacrylate have been reported in the literature, including a signal at 3.72 ppm reported by Qin et al.[23] and a signal at 3.79 ppm reported by Moineau et al.[24] This was ascribed to the effect of the ω-chlorine end group.[23] Resonances at 2.19 and 1.58 ppm correspond to -CH and -CH$_2$ backbone proton, respectively.[13] These results indicate that PDA was end-functionalized with the ω-bromine group from the catalyst.[13]

Yokota et al.[25] proposed a peculiar layered structure for the conventional comb-like polymers that was made up of several parallel alkyl side chains arranged on both sides of the main chain. They also reported that poly(*n*-alkyl) acrylates and methacrylates crystallize in hexagonal packing as characterized by a single
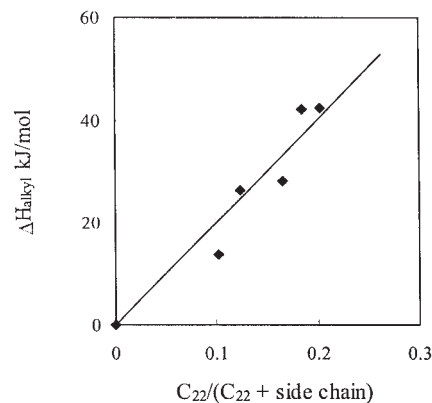
Figure 4 Plot of ΔH_{alkyl} versus fraction of C$_{22}$ content in all *n*-alkyl chains (= C$_{22}$/(C$_{22}$ + side chain)).
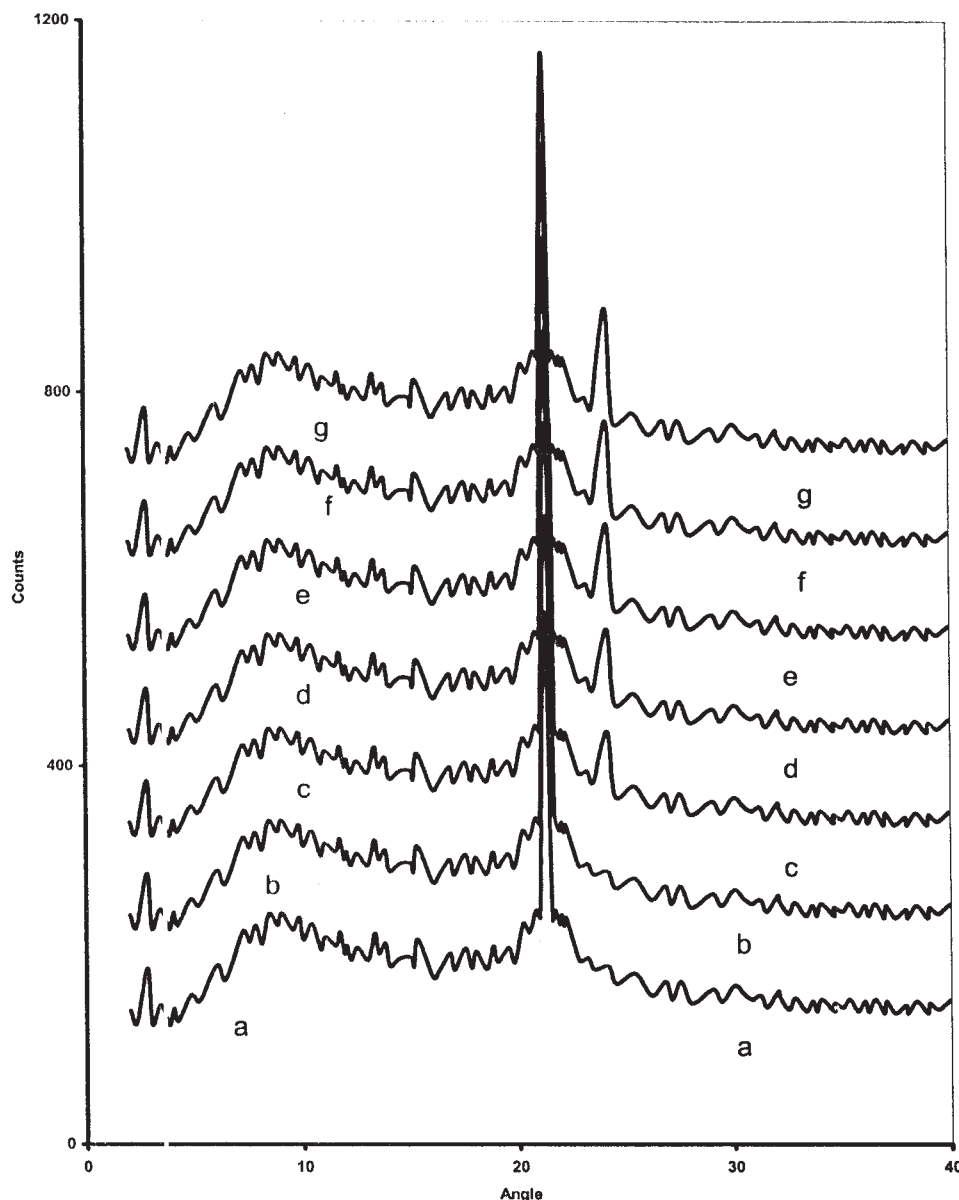
Figure 5 X-ray diffraction patterns of for PDA blends with C_{22}, measured at room temperature. Mole percent of [PDA]/[C_{22}] = (a) 100/0; (b) 90/10; (c) 75/25; (d) 50/50; (e) 30/70; (f) 20/80; (g) 10/90.

absorption band at 720 cm^{-1}. PDA prepared by the present initiation system also shows a single absorption band at 723 cm^{-1}, indicating that the long alkyl side chains of PDA are of the hexagonal type packing.

Jordan et al.[15,16] reported that polymers up to eight to nine methylene groups in the side chain tend to remain in an amorphous state and beyond this number it was observed that it participates in crystallization. Later on, Jeong et al.[26] investigated the cocrystallization behavior of poly(butylene terephthalate-co-butylene 2,6 naphthalate) random copolymers by DSC and wide-angle X-ray diffraction. The copolymers show a single melting and single crystallization peak over the entire range of copolymer composition. To investigate the cocrystallization behavior of PDA with

the corresponding fatty acid (C_{22}), DSC heating curves are recorded for blended samples that have been subjected to different thermal history. Figure 2 shows the composition dependence of DSC curves of the blended samples of PDA with C_{22} recorded in nitrogen atmosphere at heating rate of 10°C min^{-1}. The characteristic melting endotherms corresponding to the melting of the crystallites are evident in almost all samples. For pure PDA an endothermic peak occurred at 66.6°C. This is due to the crystal reorganization during the heating processes. According to Jordan et al.,[15,16] only the outer paraffinic methylene groups were present in the crystal lattices of n-alkyl (acrylates). With 25 mol % of C_{22} content, another endothermic peak is observed at higher temperature re-
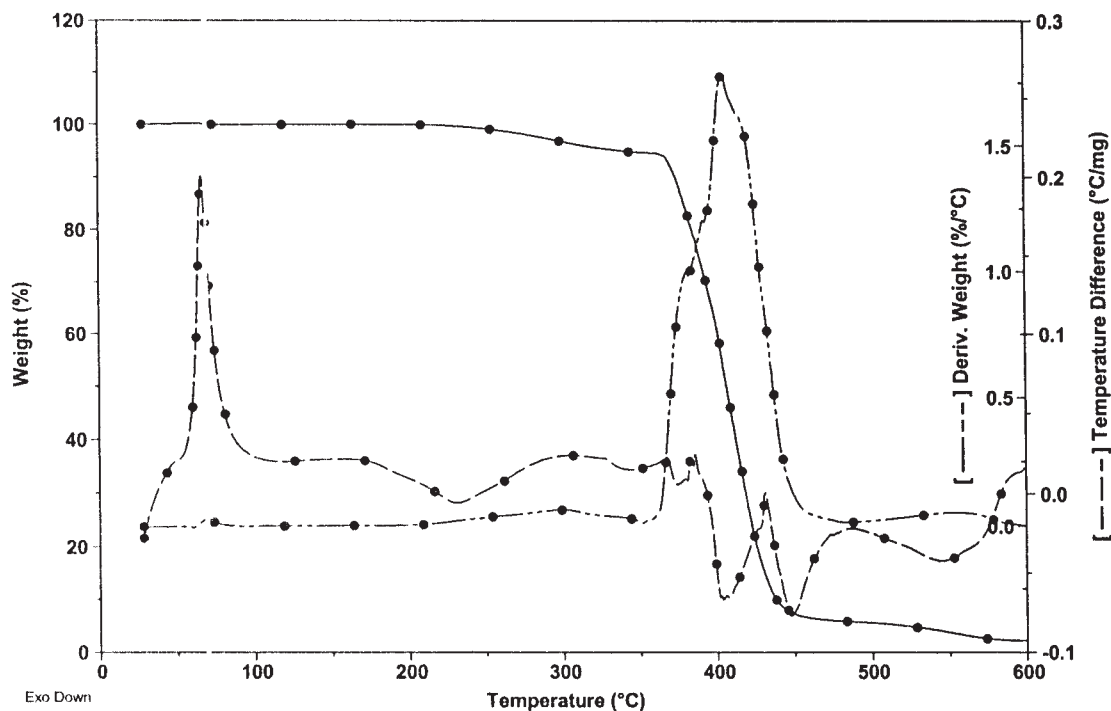
Figure 6 Thermogravimetric analysis of PDA recorded in nitrogen atmosphere at a heating rate of 10°C min^{-1}.

gion. With the increase of C_{22} content, the position of the peak moved toward the pure C_{22} (78.5°C). Shapes and temperatures of the transition peaks vary with the changing C_{22} content. Its height and temperature increase with C_{22} content and temperature approaches the crystallization point of pure C_{22}. The plot of crystallization temperature against mole fraction of C_{22} content indicates the formation of a new crystalline form at 25 mol %, and eutetic crystallization of the new crystalline form with the crystallite of PDA occurs in the range of 0–25 mol %. The heat of crystallization for 1 mol of docosyl side chain, ΔH_{side} will not change with C_{22} if the added C_{22} does not influence the crystallization behavior of the side chain.[5] The increase of ΔH_{side} with C_{22} content indicates the increase of number of methylene unit in the hexagonally packed crystalline domain (Fig. 3). So, C_{22} molecules in the solid state are cocrystallizing with *n*-docosyl side chains. Another eutectic crystallization of a new form with the crystalline of C_{22} occurs in the range of 25–100 mol %. The above interpretation for the phase behavior was also observed in the X-ray profile of the blended samples. Although the coexistence of the ordered and disordered arrangements of end-to-end form is not clearly confirmed because the peak for the C_{22} content is diffuse, the DSC curves for more than 25% of C_{22} suggest the coexistence of end-to-end form.[9] These results of DSC measurements confirm the transformation of the layered structure. The melting points (m_{p}) and the heat of fusion (ΔH_{m}) are determined from the endothermic peaks. The entropy of

fusion (ΔS_{m}) is calculated from the m_{p} and ΔH_{m} values. The relationship between the thermodynamic parameters of fusion (m_{p}, ΔH_{m}, and ΔS_{m}) and molar ratios of PDA with C_{22} is illustrated in Table I. For the first transition, the ΔH_{m} and ΔS_{m} decrease with the increase of C_{22} content and for the second transition an increase in the corresponding value is observed with the increase of C_{22}. For the state of crystalline domain containing both *n*-docosyl side chain and C_{22}, the heat of crystallization for 1 mol of *n*-alkyl chain, ΔH_{alkyl} (*n*-docosyl side chain and C_{22} molecule), is calculated. From this, it is suggested that in one *n*-alkyl chain, the cocrystallization behavior of comb-like polymer with C_{22} increases the average number of methylene units that exist in the hexagonally packed crystalline domain[5] (Fig. 4).

X-ray diffraction measurements of PDA and different blends of PDA with C_{22} are carried out at room temperature. The diffraction pattern of PDA shows a peak at about $2\theta = 21.6°$, which corresponds to an interplanar distance of 4.12 Å. The spacing at 4.12 Å corresponds to the typical hexagonally packed cylinders of *n*-alkane crystals close to their melting points. Besides this peak, the peak at 3° is also very prominent in all blended samples. In the diffraction pattern of blends with 25 mol % of C_{22} or less, only these two peaks with varied intensities are observed. With more than 25 mol % of C_{22}, an additional peak appeared at $2\theta = 24.1°$ and the intensity of the peak increased with the increase of C_{22} content (Fig. 5). The C_{22} molecule crystallizes into some polymorphs and the newly ap-

peared peaks can be assigned to the crystallite in the C-form of C_{22}.[9] In the samples containing less than 25 mol % of C_{22}, the absence of X-ray diffraction peaks and DSC transition corresponding to the pure C_{22} confirms the existence of only a hexagonally packed crystalline lattice.

The primary method for monitoring pyrolysis of polymers is thermogravimetric (TGA) analysis. TGA is used to determine the chemical structure and the pyrolytic properties of polymers by measuring mass volatilized as function of time. Although the chemical reactions underlying the pyrolysis are known, the usual method for interpreting TGA data are based on simplified kinetics models.[27] Thermal degradation (Fig. 6) of PDA proceeded in a one-step reaction, i.e., T_{ini} = 220–290°C and T_{max} = 340–450°C. The weight residue at 550°C is below 2%, suggesting that depolymerization of PDA occurs similar to PMMA. Kinetic parameters of PDA are calculated from nonisothermal TG curves using nonmechanistic equations of Freeman and Carroll[28] and Flynn and Wall[29] and the results are found to be in good agreement with each other. The average activation energy for the decomposition of PDA is 85.23 kJ mol^{-1}.

CONCLUSIONS

X-ray diffraction and thermal studies have contributed to a better understanding of the overall blend structure of PDA with n-docosanoic acid (C_{22}). The morphology of polymer blends is dependent on the crystallization condition. For blended samples, DSC measurements suggest the existence of another crystalline form induced by the addition of n-docosanoic acid. The characteristic melting endotherms that correspond to the melting of the crystallites are observed from the cocrystallization behavior of PDA with C_{22}. Thermal degradation of PDA proceeded in a one-step reaction. The TGA curves show an increase in thermal stability and give main chain scission in the region of 340°C.

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