Hydrogen-Bonded Thermostable Liquid Crystalline Complex Formed by Biodegradable Polymer and Amphiphilic Molecules

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ABSTRACT: We report a simple method to prepare biodegradable polymer−amphiphile complexes by solution mixing of poly(propylene carbonate) (PPC) with octadecanoic acid (OA). The complexes were characterized by combination of thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS), polarizing optical microscopy (POM), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FT-IR). Compared with the amorphous PPC copolymer, the PPC−OA-*x* complexes show excellent thermal stability and form thermotropic liquid crystalline state without rigid mesogenic units. The corresponding mechanism has been proposed to elucidate the observed phenomena. The stabilization effect induced by hydrogen-bonding interactions between PPC and OA molecules is responsible for the thermostability and formation of liquid crystalline state. The present findings may extend the applications of such biodegradable aliphatic polycarbonate by improving its glass transition temperature and thermoplastic processability.

Introduction

It is well-known that carbon dioxide (CO_2) is generally regarded as the main factor to cause greenhouse effect.[1] Thus, proper utilization and disposal of CO_2 have been the subject of researchers all over the world. Since Inoue and co-workers synthesized aliphatic polycarbonate by copolymerization of CO_2 with epoxides using organometallic compounds as catalysts in 1969,[2] extensive studies have been carried out in this area because of the effective fixation of CO_2 and the complete biodegradability of the resulting copolymers. Over the past several decades, significant achievements have been made in developing highly active catalytic systems for the CO_2/epoxides copolymerization, which were detailedly summarized in several related reviews.[3] Compared with universal thermoplastics, however, aliphatic polycarbonate as a kind of amorphous polymers shows some disadvantages such as lower glass transition temperature, noncrystallinity, and being prone to degrade when subjected to thermal treatment.[4] These blemishes lead to the weak mechanical properties and poor thermal processability, which limits the practical application of this biodegradable material. Although many modification methods were tried to enhance the performances of the aliphatic polycarbonate,[5] very few progresses have been achieved.

In recent years, supramolecular polymer−amphiphile complexes based on specific noncovalent interactions such as hydrogen bonding, ionic interactions, etc., have received considerable attention due to the simple fabrication and the specially potential functions.[6] Earlier reports have revealed that the fatty acids, as a kind of common amphiphilic compounds, can form comblike liquid crystalline complexes without mesogenic units when associating with some polymers containing amino groups like poly(ethylenimine) (PEI).[7−12] The PEI−fatty acid (such as stearic acid) systems exhibit supramolecular thermotropic smectic phase, which was confirmed using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) methods.[7,8,11,12] Furthermore, the association mode of these complexes was investigated by Fourier transform infrared spectroscopy (FT-IR), and it was found that the formation of thermotropic mesophase can be attributed to the ionic interactions between amine and carboxyl groups which play an important role in stabilizing the liquid crystals even at temperatures above melting temperature (T_m) of the fatty acids.[8,11,12]

In the present work, we report the preparation and structural characterization of biodegradable polymer−amphiphile complexes using poly(propylene carbonate) (PPC) and octadecanoic acid (OA), which represent characteristic aliphatic polycarbonate and amphiphilic compound, respectively. These supramolecular complexes show excellent thermal stability, thermotropic liquid crystalline character, and enhanced glass transition compared with the amorphous PPC copolymer. To the best of our knowledge, it is unique that ordered supramolecular thermotropic liquid crystal is formed by biodegradable polycarbonate and amphiphilic molecules through simple complexation.

Experimental Section

Materials. PPC copolymer was supplied by Inner Mongolia Mengxi High-tech Materials Co. (China). The residual byproduct

Table 1. Composition and Phase Transition of the PPC−OA-*x* Complexes

sample	w_{feed}[a]	x_{cal}[b]	x	C (wt %)	T_g (°C)	T_i[c] (°C)	ΔH_i[d] (J/g)
PPC−OA-0.0028	0.01	0.0036	0.0028	47.08	37.9		
PPC−OA-0.0120	0.05	0.0189	0.0120	47.80	38.7	126.6	5.67
PPC−OA-0.0155	0.10	0.0399	0.0155	48.07	38.2	126.4	6.22
PPC−OA-0.0208	0.20	0.0897	0.0208	48.46	38.6	127.4	5.18
PPC−OA-0.0217	0.30	0.1540	0.0217	48.52	38.4	128.1	6.02

[a] Weight feed ratio of OA to PPC. [b] Calculated molar ratio of OA to carbonate group of PPC. [c] Peak value for phase transition. [d] Enthalpy of isotropization.

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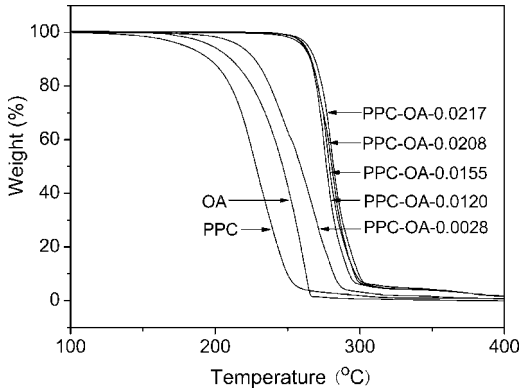

Figure 1. TG thermograms of the PPC−OA-*x* complexes compared with those of pure OA and PPC.

Table 2. Thermal Stability for PPC, OA, and the PPC−OA-*x* Complexes

sample	$T_{5\%}$	T_{max}[a]	$T_{95\%}$
PPC	179.0	205.1	257.4
OA	197.5	232.2	264.5
PPC−OA-0.0028	217.0	229.9	287.2
PPC−OA-0.0120	261.1	266.0	310.0
PPC−OA-0.0155	262.1	268.3	311.8
PPC−OA-0.0208	260.5	268.6	326.1
PPC−OA-0.0217	264.1	270.2	313.7

[a] T_{max} is defined as the maximum weight-loss temperature.

in the copolymer was removed by a repeated dissolution/precipitation procedure with acetone as a solvent and methanol as a nonsolvent. The weight-average molecular weight and the polydispersity index of the purified PPC were determined by gel permeation chromatography (GPC) as 1.8×10^5 and 2.44, respectively. The carbonate unit content of the purified copolymer was 97.2%, being estimated from the ^{1}H NMR spectrum according to the formula described in the literature.[13,14] OA (Grade 1) was purchased from Sigma-Aldrich Co. and used as received. All other chemicals were analytical reagents and refined according to the standard procedures.

Sample Preparation. PPC and OA were separately dissolved into acetone at a concentration of 5% (w/v). The resultant solutions were mixed in desired weight proportions of OA/PPC (1/99, 5/95, 10/90, 20/80, and 30/70), stirred at room temperature for 3 h, and then cast onto Petri dishes. The precomplexes were dried under vacuum at 65 °C for 48 h. Subsequently, the dried preproducts were purified with hot ethanol for 0.5 h to ensure complete removal of all unbound OA molecules and dried under vacuum at 65 °C until constant weight. The final complexes were kept in a desiccator before use. The carbon content *C* (wt %) of the complexes was determined with a Thermo Electron Flash EA1112 elemental analyzer, and the composition *x* (molar ratio of OA to carbonate group of PPC) was calculated (Table 1).

Sample Characterization. Thermogravimetry analysis (TGA) test was carried out with a Perkin-Elmer Pyris 1 TGA thermal analyzer under a nitrogen atmosphere at a heating rate of 20 °C/min from 20 to 600 °C. Differential scanning calorimetry (DSC) experiments were performed on a Mettler DSC 882e calorimeter under a nitrogen atmosphere. The samples were first heated at a rate of 20 °C/min from 25 to 140 °C to remove thermal history and then cooled down at a rate of 10 °C/min from 140 to −30 °C, followed by the second heating process from −30 to 140 °C at a rate of 10 °C/min. Wide-angle X-ray diffraction (WAXD) patterns for melt-pressed pellets of samples were recorded on a Rigaku D/max-2500 diffractometer using Cu Kα radiation ($\lambda = 0.1541$ nm) in the 2θ scan range of 3−40° at ambient temperature. Small-angle X-ray scattering (SAXS) measurement of complex powders was performed with an Anton Paar SAXSess system using Cu Kα radiation ($\lambda = 0.1541$ nm) at room temperature. The scattering vector *s* ranged from 0.1 to 1.5 nm^{-1}, where $s = (2/\lambda) \sin \theta$. The microscopic structure of the complexes was assessed by transmission electron microscopy (TEM) using a JEOL JSM-2200FS model operated at 200 kV. The samples were prepared by adding one drop of 0.3% (w/w) acetone solution of the complexes on the

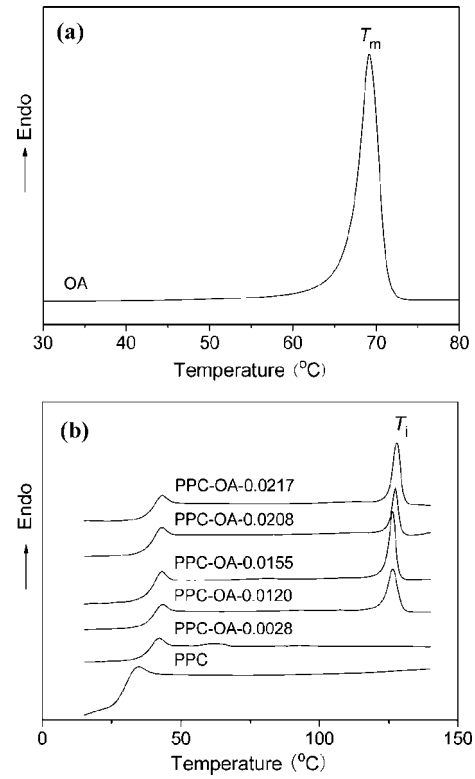

Figure 2. DSC traces of PPC−OA-*x*complexes during the second heating at a rate of 10 °C/min compared with those of pure OA and PPC.

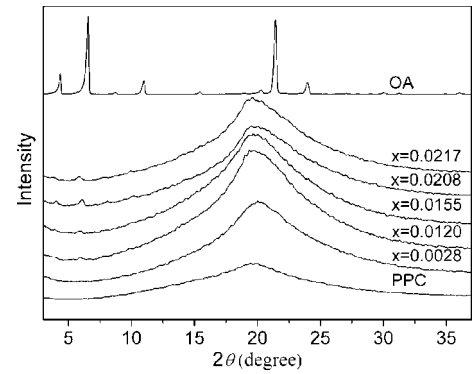

Figure 3. WAXD profiles of OA, PPC, and the PPC−OA-*x* complexes recorded at room temperature.

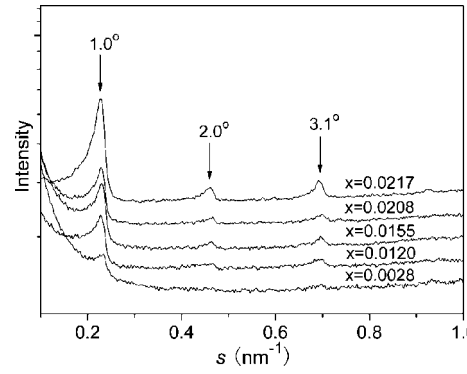

Figure 4. SAXS patterns of the PPC−OA-*x* complexes recorded at room temperature.

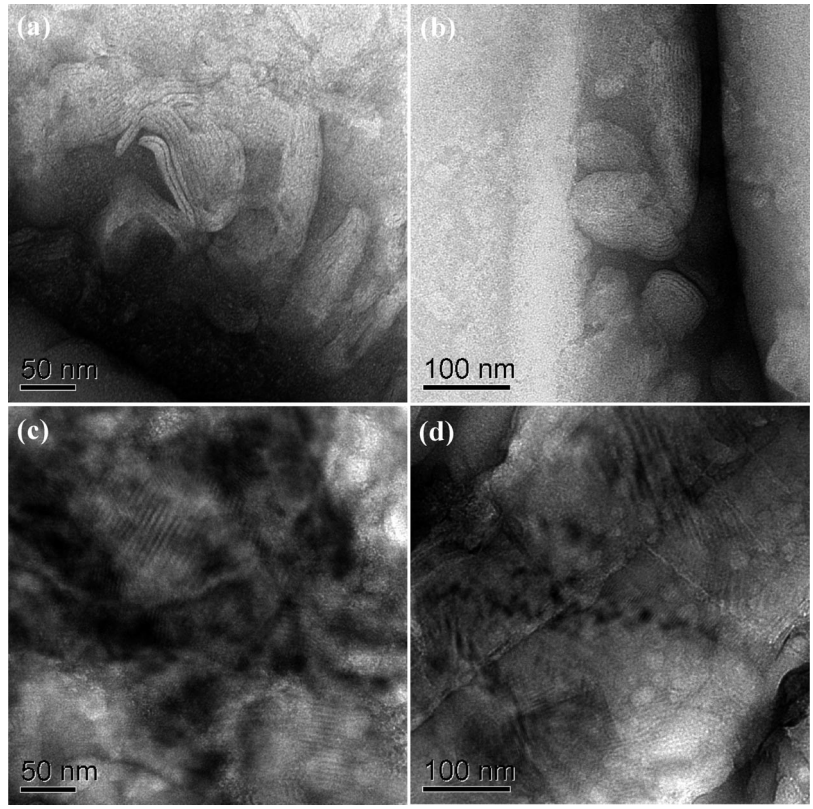

Figure 5. TEM micrographs of (a, b) PPC−OA-0.0208 and (c, d) PPC−OA-0.0217 complexes.

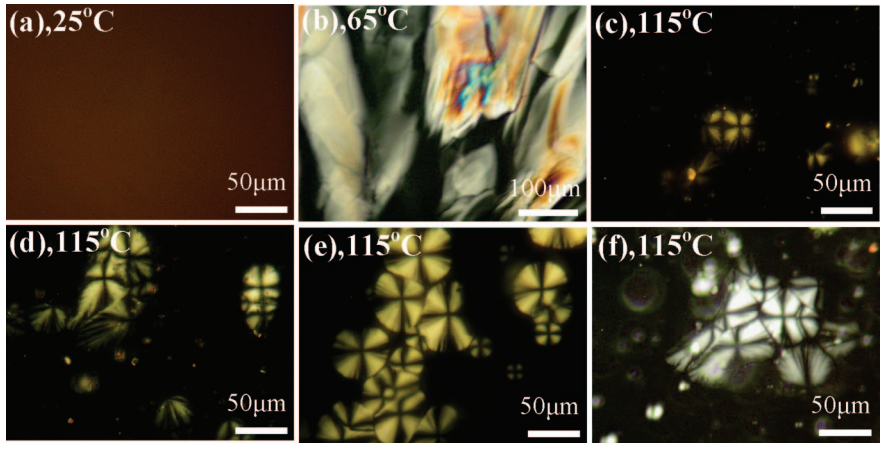

Figure 6. Polarizing optical micrographs for (a) PPC and (b) OA compared with those of ((c) $x = 0.0120$, (d) $x = 0.0155$, (e) $x = 0.0208$, (f) $x = 0.0217$) sheared PPC−OA-x complex film taken during the cooling process.

carbon-coated copper grids and then stained with ethanol solution of uranyl acetate to enhance contrast. The mesomorphous phase of the complexes was observed with a Nikon Eclipse E600 polarizing microscope equipped with a Linkam CSS450 temperature-controlled shearing hot stage. The samples were melted at 140 °C, then sheared into films with a thickness of ca. 30−40 μm, and quickly cooled down to room temperature. The obtained films were subjected to a heating and then cooling process at a rate of 1 °C/min, and the polarizing optical microscopic (POM) micrographs were taken by a Nikon E4500 camera. FT-IR spectra of samples were recorded on a Bruker EQUINOX 55 spectrometer. A resolution of 2 cm^{-1} was chosen, and 64 scans were signal-averaged. Temperature-variable FT-IR measurements were carried out in a SPECAC variable temperature cell directly mounted in the spectrometer. The spectra were collected from 30 to 130 °C with the heating rate controlled at ca. 1 °C/min. The samples were equilibrated for ca. 3 min before measurement at each temperature point.

Results and Discussion

According to the data listed in Table 1, the actual composition x of the PPC−OA-x complexes is always lower than the expected value x_{cal} (Table 1). This is due to the fact that only partial OA were bound to PPC molecules, and the unbound OA molecules were removed from the precomplexes in the purification process.

The thermal properties of the complexes were characterized using TG and DSC methods. TG thermograms (Figure 1) indicate that the PPC−OA-x complexes are more thermally stable compared with pure OA and PPC. As shown in Table 2, the 5% weight-loss temperature (denoted as $T_{5\%}$) of PPC and OA are 179 and 198 °C, respectively. However, all the complexes exhibit a much higher $T_{5\%}$ in the range of 217−264 °C, which means that the thermal stability of PPC has been

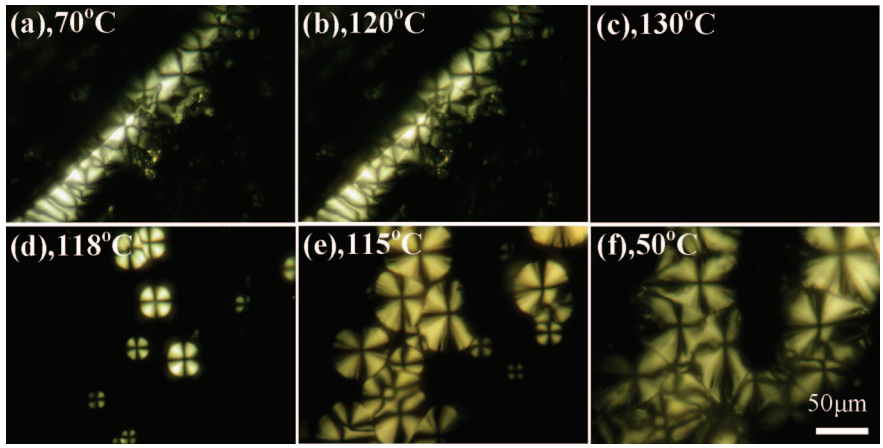

Figure 7. Polarizing optical micrographs taken during the (a−c) heating and (d−f) cooling process for sheared PPC−OA-0.0208 complex film.

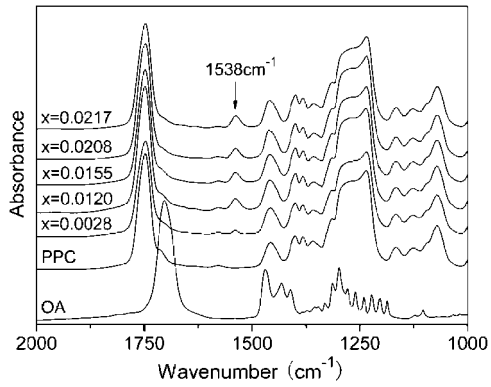

Figure 8. FT-IR spectra of the PPC−OA-x complexes at room temperature compared with those of pure OA and PPC.

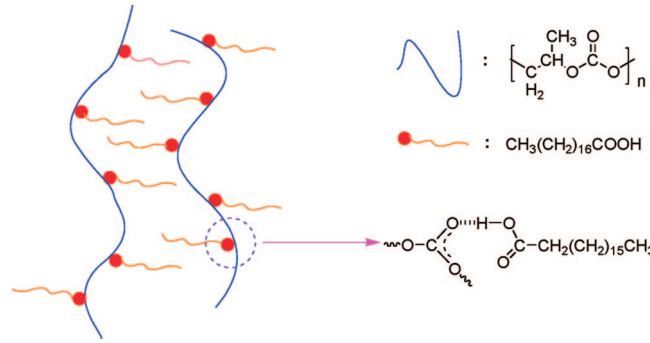

Figure 9. Schematic illustration of hydrogen-bonding interaction between carbonate group and carboxyl group in the PPC−OA-x complexes.

improved greatly and this copolymer may have enhanced thermoplastic processability.

DSC traces (Figure 2) show that OA give only one sharp melting peak at 69.1 °C (ΔH_m = 215.11 J/g) during the heating process, while the PPC−OA-x complexes (except x = 0.0028) exhibit only one endothermic peak within a temperature range far beyond melting temperature (T_m) of pristine OA. In addition, the glass transition temperature (T_g) of PPC increased from 30.4 °C to ca. 38 °C when it was bound by OA. As it has been reported previously that there is a thermotropic liquid crystalline state existing above T_m of OA in the PEI−OA complexes,[7,8,11,12] we temporarily attribute the endothermic peak for PPC−OA complexes at ca. 126−128 °C to the isotropic temperature (T_i), corresponding to a transition from a liquid crystalline phase to an isotropic phase. In order to further elucidate the DSC results, WAXD, SAXS, TEM, and POM measurements were combined to verify the existence of the mesomorphous state in the PPC−OA complexes.

WAXD profiles of OA, PPC, and the complexes are displayed in Figure 3. Pure OA displays two sharp diffraction peaks at 2θ = 21.4 and 24.0° (correspondingly d = 0.41 and 0.37 nm, respectively), indicating that it crystallizes in the orthorhombic form.[8,11,12] In contrast, PPC and the complexes only give a wide-angle diffuse halo at ca. 2θ = 20°, which indicates a noncrystalline state existing in these complexes. Nevertheless, whether the long-range ordered structures exist in the complexes needs to be corroborated by SAXS results.

SAXS patterns of the PPC−OA-x complexes are illustrated in Figure 4. There are at least three reflections at equidistant positions in s scale as 1:2:3, which is characteristic of lamellar mesomorphous structure.[6] This lamella consists of n-alkyl chain layer of the bound OA and the polymer chain layer with the polar heads of the amphiphiles. While the length of fully extended OA chain is 2.4 nm,[12] the long period of the complexes is ∼4.3 nm, corresponding to the scattering peak at s = 0.23 nm^{-1}, indicating that the alkyl tails of OA are interdigitated in the complexes.

Figure 5 displays the TEM micrographs of the PPC−OA-x complexes with relatively high OA content (x = 0.0208 and 0.0217). It clearly shows that the complexes have lamellar structures with a characteristic period of ca. 4.1 nm, which is in good agreement with the SAXS results. The layer of PPC chains with carboxyl group of OA in the lamella is dark due to the staining effect of uranyl acetate.

As presented in Figure 6a, no birefringent patterns could be observed under crossed polarizers of the microscope for PPC film due to its amorphous state, which is consistent with the DSC and WAXD results. When OA sample was cooled from the melt, lots of large crystal quickly spread through the visual field (Figure 6b), which demonstrates that pure OA cannot form liquid crystalline phase as reported in previous papers.[7,12] Surprisingly, POM micrographs of the PPC−OA-x complexes show clear liquid crystal textures, thus giving a direct proof of the formation of thermotropic mesophases (Figure 6c−f). In order to further explore the mesomorphous structure formed in the complexes, the PPC−OA-0.0208 complex was taken as an example to show the changes occurred during the heating and cooling process (Figure 7). A smectic phase with the characteristic of focal conic texture was observed at room temperature and remained almost unchanged as being heated until 120 °C (Figure 7a,b). With temperature further increasing, the liquid crystal gradually turned into isotropic fluid, and the observation field became completely black at 130 °C (Figure 7c). This phenomenon supports the assumption that the endothermic peak in the DSC heating scan for PPC−OA-x complexes arises from

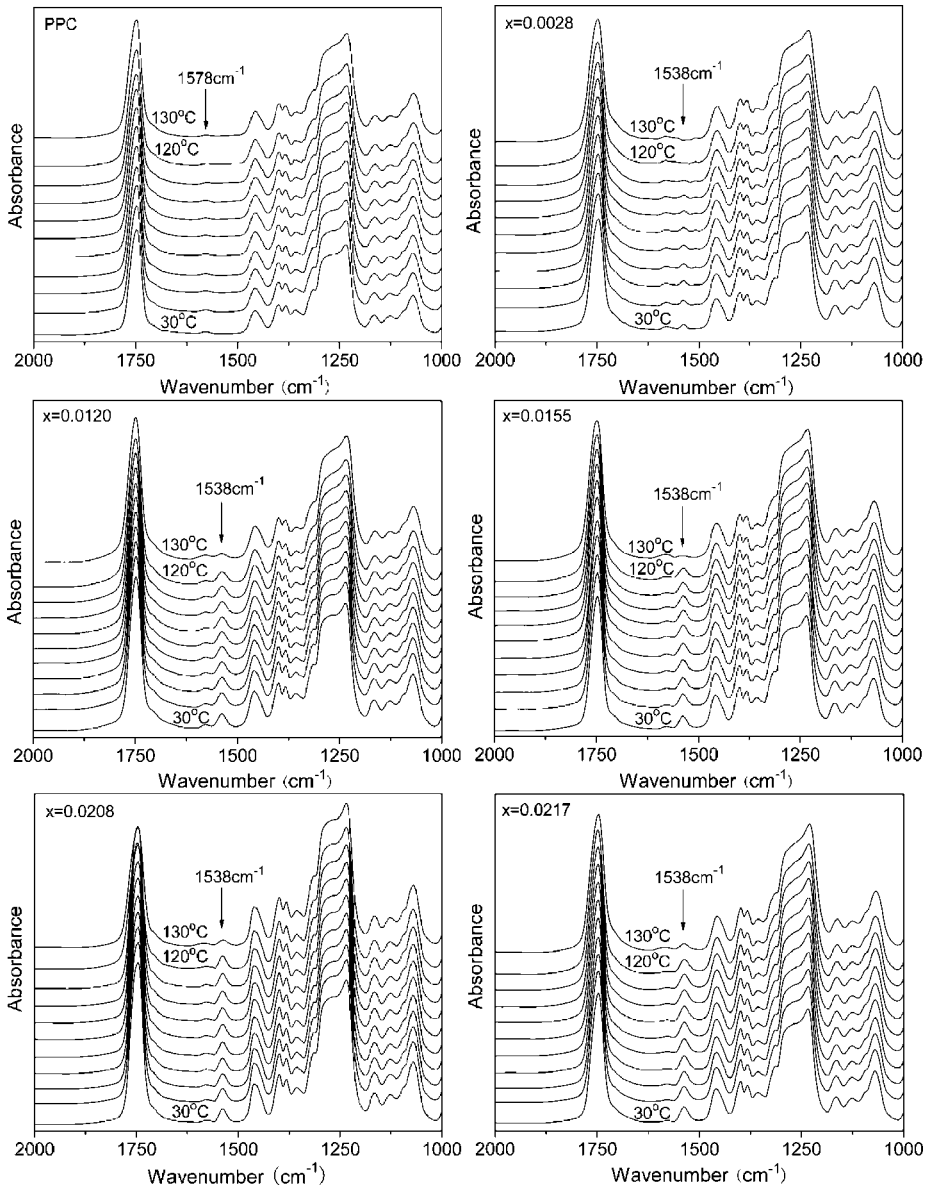

Figure 10. Variable-temperature FT-IR spectra of PPC and the PPC−OA-*x* complexes during the heating process. From bottom to top, the temperatures rise up from 30 to 130 °C at an interval of 10 °C.

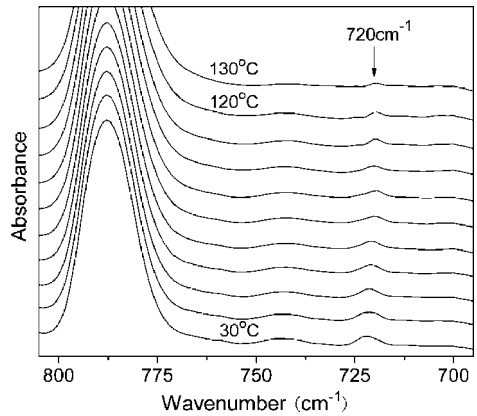

Figure 11. Variable-temperature FT-IR spectra of PPC−OA-0.0208 complex during the heating process. From bottom to top, the temperatures rose up from 30 to 130 °C at an interval of 10 °C.

isotropization of the mesomorphous phase. Thereafter, the complex was cooled down from the isotropic melt, and many spherulitic textures with a typical Maltese extinction cross appeared in the polymer matrix at 118 °C (Figure 7d). Subsequently, the spherulites grew up and collided with each other (Figure 7e), and finally a focal conic texture (Figure 7f) was formed again in the complex film. It should be noted that the spherulitic textures can be regarded as Dupan cyclides which also indicates the existence of smectic phase.[8]

Although we can confirm the existence of the smectic liquid crystal in the PPC−OA-*x* complexes by combination of DSC, WAXD, SAXS, TEM, and POM techniques, the formation mechanism of the liquid crystalline state is still unclear. Therefore, the complexes were investigated by FT-IR spectroscopy, since it is efficient in probing intermolecular interactions. The IR spectra of pure OA, PPC, and PPC−OA complexes are presented in Figure 8. Pure OA showed an absorption band at 1703 cm^{-1}, corresponding to the stretching vibration of the C═O group for the −COOH group of the carboxylic acid dimer.[15] PPC displayed two strong bands at 1747 and 1250 cm^{-1}, assigned to the stretching vibrations of the C═O group and C−O−C bond of the carbonate group, respectively.[13,14] However, the dimer band at 1703 cm^{-1} could not be observed in the spectra of the PPC−OA-*x* complexes, suggesting all dissociated OA molecules have been removed through purifica-

tion with hot ethanol. Although the absorption peak position of carbonyl group in PPC almost keeps unchanged, an obvious new band appears approximately at 1538 cm^{-1} in spectra of the complexes. Since the ionic PEI−OA complex shows the C═O stretching vibration of the ionized carboxylate (COO^-) at ca. 1552 cm^{-1},[8,9,11] this new band 1538 cm^{-1} in the present work cannot be assigned to intermolecular ionic interactions in the PPC−OA-*x* complexes. Recently, it has been reported that strong hydrogen-bonding interactions formed between the ester group and the carboxylic acid group in polymer blends at the expense of the self-association of the carboxylic acids.[16,17] On the basis of the above literatures, a schematic diagram was given for the hydrogen bonds formed in the PPC−OA complexes (Figure 9). The carboxylic groups of bound OA act as the proton donor, while the carbonyl group of PPC plays the role of proton acceptor. Therefore, PPC associates with OA via hydrogen-bonding interactions, leading to the construction of "semirigid" aggregates similar to rodlike mesogens.[18] The enhanced rigidity confines the motion of molecular chains in the complex, which consequently raises T_g of PPC copolymer due to the stiffening of polymer chains.[6] On the other hand, the long alkyl chains of bound OA may play a similar role as a flexible "spacer" group.[11] The above two moieties in the complex resemble the counterparts in conventional liquid crystals and facilitate the mesomorphous phase formation. Obviously, the hydrogen bonds formed in the complexes contribute to the appearance of the new peak at 1538 cm^{-1}. In addition, the relative intensity of the 1538 cm^{-1} band increases with the increase of *x* values (Figure 8), which might be induced by the formation of stronger hydrogen-bonding interactions at higher content of carboxylic acid groups in the complexes. It has been reported that the unzipping degradation of poly(alkylene carbonate) originates from a nucleophilic attacking of the carbonyl group of polymer by terminal hydroxyl group.[19] Since the carbonyl group of PPC forms hydrogen bonds with carboxylic group of OA, the chain unzipping process is hindered and the thermal degradation of the PPC−OA complexes is restricted to chain scission reaction that occurs at higher temperature than chain unzipping.[19] Therefore, the thermal stability of PPC is improved significantly as shown in the TG thermograms.

To further investigate the hydrogen-bonding interactions existing in the PPC−OA-*x* complexes, variable-temperature FT-IR spectroscopy was selected as an effective characterization method (Figures 10 and 11). As shown in Figure 10, the intensity of the band at 1538 cm^{-1} remained unchanged until the temperature exceeded 120 °C (except $x = 0.0028$), which can be reasonably related to the hydrogen-bonding interactions in the complex. The presence of hydrogen bonds in the complex plays a key role in stabilizing the thermotropic liquid crystalline phase and results in the enhanced thermal stability of PPC. Above 120 °C, the intensity of this peak decreased dramatically and almost disappeared at 130 °C, indicating the hydrogen bonds were destroyed. These results agree well with the phase transition behavior detected by DSC and POM.

FT-IR studies crystallization of polyethylene and *n*-paraffins at room temperature have revealed the different crystalline modifications of long alkyl chains.[20,21] A doublet peak at 720/730 cm^{-1} is assigned to the methylene rocking vibration (γ_{CH_2}) of orthorhombic packing of the hydrocarbon chains, while a single band in this region is correlated with hexagonal or triclinic packed chains. Moreover, a single band at 723 cm^{-1} corresponds to γ_{CH_2} of amorphous state. As can be seen in Figure 11, the appearance of only one single peak at 723 cm^{-1} in the IR spectra of PPC−OA-0.0208 complex at 30 °C indicates that the long alkyl chains in the complex are in the amorphous state, which may account for the lack of crystal−melt transitions in the DSC traces. With the increase of temperature, the band at 723 cm^{-1} gradually shifted to lower wavenumber, and its absorbance decreased correspondingly. The weak absorption at 720 cm^{-1} at high temperatures is characteristic of the aliphatic chains in the melt state.[21]

Conclusions

In this study, PPC−OA complexes have been successfully prepared through a simple method of solution mixing. The excellent thermal stability of the PPC−OA-*x* complexes may be attributed to the formation of hydrogen-bonding interaction between PPC and OA, which may also be responsible for the stabilization of thermotropic liquid crystals in the complexes. These findings will facilitate development and wide application of this biodegradable polycarbonate in the future.

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