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Preparation and thermal degradation kinetics of terpolymer poly(ε-caprolactone-co-1,2-butylene carbonate)

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Poly(ε-caprolactone-co-1,2-butylene carbonate) (PBCCL) was successfully synthesized *via* terpolymerization of carbon dioxide, 1,2-butylene oxide(BO) and ε-caprolactone (CL). A polymer-supported bimetallic complex (PBM) was used as catalyst. The influences of various reaction conditions such as reaction content, reaction time and reaction temperature on properties of terpolymers were investigated. When CL content increased, the viscosity-average molecular weights (M_v), glass transition temperature (T_g) and decomposition temperature (T_d) of PBCCL improved relative to those of poly(1,2-butylene carbonate) (PBC). Prolonging the reaction time resulted in increase in M_v and T_g. As reaction temperature increased, the molar fractions of CL (f_{CL}) increased obviously. When the reaction temperature went beyond 80 °C, the resulting copolymers tended to be crystalline. The thermal properties and degradation behaviors of PBCCL were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The apparent activation energy and thermal degradation model of PBCCL was estimated by means of Ozawa–Flynn–Wall method and Phadnis-Deshpande method, respectively. The results showed that T_g and T_d of the terpolymer PBCCL were much higher than those of PBC. The thermal degradation behavior of PBCCL was evidenced by one-step thermal degradation profile. The average apparent activation energy is 77.06 kJ/mol, the thermal degradation kinetics follows the power law thermal decomposition model.

1. Introduction

Carbon dioxide is currently regarded as an environmental pollutant that causes the greenhouse effect [1]. Since the pioneering work of Inoue in 1969 [2], the synthesis of aliphatic polycarbonates from carbon dioxide and epoxides has attracted longstanding interest as potential method of using CO_2 [3,4]. Aliphatic polycarbonate represents one family of biodegradable materials used for biomedical applications, such as drug carriers and implant materials because of their good biocompatibility, low toxicity, and biodegradability [5]. In the past decades, increasing attention has been paid to the modification and application of polycarbonates [6–8]. Aliphatic polycarbonates can be modified by functional groups, such as ester [9–11], carboxyl [12] to improve their thermal properties and degradability. In recent years, aliphatic polycarbonates have been explored in the search and design of new polyester-related structures for medical applications [13]. Poly (ε-caprolactone) (PCL) is a semicrystalline linear resorbable aliphatic polyester, has been extensively investigated for use as implantable or injectable biodegradable carriers for the controlled release of active agents [14]. The thermal properties and biodegradability of PCL can be modified by copolymerization of ε-caprolactone with other monomers [15–18], PCL is also compatible with various polymers [19]. In our earlier work, PBCCL was synthesized *via* terpolymerization of carbon dioxide, 1,2-butylene oxide and ε-caprolactone, the degradability and thermal properties of the PBCCL was higher than those of PBC, the application as matrix polymers for controlled drug delivery systems has also been investigated [20]. Thermal properties are one of the most important properties for polymeric materials. Thus, the research of thermal stability and thermal degradation kinetics may be significant to production and application.

In the present work, the influences of various manufacturing parameters including reaction content, reaction time and reaction temperature were investigated to optimize the process variables of terpolymerization. In order to research the thermal stability, the apparent activation energy and the kinetics of thermal degradation mechanism of PBCCL, the thermal properties and degradation behaviors of PBCCL were investigated by DSC and TGA.

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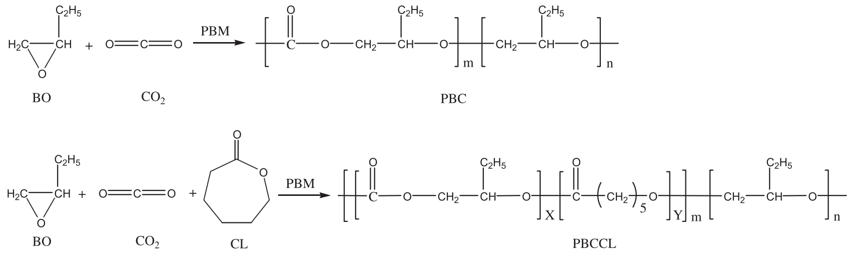

Scheme 1. Synthesis and structure of PBC and PBCCL.

Table 1
Influence of BO:CL molar ratio on the properties of copolymers.

Copolymer	BO:CL (in molar)	Composition[a] (molar fraction in %)			Yield (g/g of cata.)	[η] (dL/g)	$M_v \times 10^4$	$M_w/M_n \times 10^4$	PDI	T_g (°C)
		f_{CO_2}	f_{BO}	f_{CL}						
PBC	5:0	44.98	55.02	0.00	38.33	0.455	3.28	3.65/2.70	1.35	1.4
PBCCL-1	5:1	38.25	52.29	9.46	47.12	0.558	4.23	5.24/2.67	1.96	41.2
PBCCL-2	5:2	36.68	50.70	12.62	53.08	0.714	5.76	6.84/3.76	1.82	46.0
PBCCL-3	5:3	35.66	49.75	14.59	56.84	0.745	6.08	7.75/4.38	1.77	46.8
PBCCL-4	5:4	34.55	50.43	15.02	53.89	0.763	6.26	7.91/5.46	1.45	47.3
PBCCL-5	5:5	34.21	50.32	15.47	51.36	0.752	6.15	7.62/4.67	1.63	47.0

Reaction conditions: $T = 70$ °C; $t = 24$ h; 0.5 mol BO; 1.0 g catalyst.

[a] The molar fractions of CO_2, BO and CL calculated by integrating areas of ^1H NMR spectra of PBC and PBCCL.

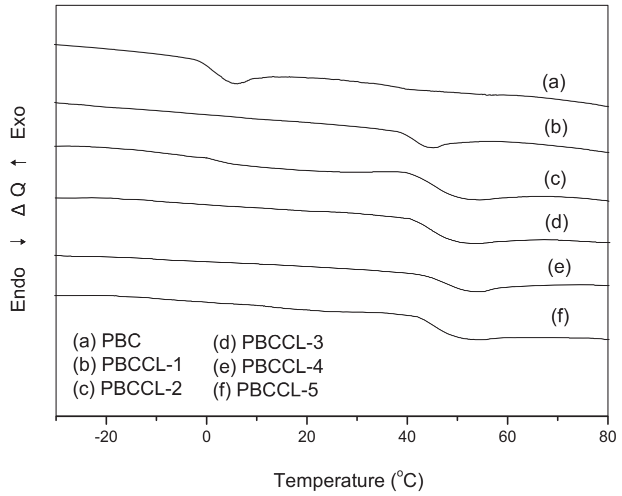

Fig. 1. DSC curves of PBCCL prepared from different BO:CL molar ratio.

2. Experimental

2.1. Materials

BO (Shanghai Chemical Reagents Co., A.R. grade) and toluene (Hengyang Organic Chemical Reagents Plant, A.R. grade) were further purified by 0.4 Å molecular sieves prior to use. CL (A.R. grade) was purchased from Daicel and distilled before use. CO_2 and N_2 (purity more than 99.5%) were purchased from Hunan Special Gas Factory (China). The P-$Zn[Fe(CN)_6]_aCl_{2-3a}(H_2O)_b$ (PBM) catalyst was obtained from the Guangzhou Institute Chemistry of the Chinese Academy of Sciences, it was synthesized according to the literature [21]. All other reagents and solvents were of analytical grade and used without further purification.

2.2. Preparation and purification of copolymers

PBCCL was synthesized in similar procedure to that of PBC, except that CL was added into the autoclave pro rata to BO. The reaction of PBC and PBCCL is shown in Scheme 1. The synthesis and characterization of PBC and PBCCL were detailed in our earlier work [20]. Briefly, PBC and PBCCL were carried out in a 300 ml stainless steel autoclave equipped with a magnetic stirrer. The reactor was

Table 2
Influence of reaction temperature on the properties of copolymers.

Copolymer	Temperature (°C)	Composition[a] (molar fraction in %)			Yield (g/g of cata.)	[η] (dL/g)	$M_v \times 10^4$	$M_w/M_n \times 10^4$	PDI	T_g (°C)	T_m (°C)
		f_{CO_2}	f_{BO}	f_{CL}							
PBCCL60	60	42.56	51.29	6.15	37.88	0.701	5.63	6.25/3.20	1.95	46.0	–
PBCCL70	70	35.66	49.75	14.59	56.84	0.745	6.08	7.75/4.38	1.77	46.8	–
PBCCL80	80	29.61	41.82	28.57	61.55	0.539	4.05	5.63/2.78	2.03	−45.7	46.5
PBCCL90	90	22.15	36.47	41.38	57.70	0.518	3.86	5.16/2.10	2.46	−51.2	50.8

Reaction conditions: $t = 24$ h; 0.5 mol BO; 0.3 mol CL; 1.0 g catalyst.

[a] The molar fractions of CO_2, BO and CL calculated by integrating areas of ^1H NMR spectra of PBCCL.