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Synthesis and properties of novel thermotropic liquid crystalline copoly(ester-imide)s

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Abstract

Four novel copoly(ester-imide)s based on 3,3′,4,4′-biphenyltetracarboxylic dianhydride, bis(trimellitic acid anhydride) phenyl ester and di-p-aminophenyl ester of dicarboxylic acids were synthesized via two-step method in order to investigate whether two imide mesogenic units with different conformation and polarity could control the formation of LC-phase. Polarizes light microscopy (PLM) and differential scanning calorimetry (DSC) have shown that three polymers formed the nematic phase with "thread schlieren texture" and a polymer formed the nematic phase with "Inversion walls texture".

Keywords: Copoly(ester-imide); Inversion walls texture; Mesogenic unit; Thermotropic liquid crystalline

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Two basic questions of liquid crystalline polymer are the stabilization of LC-phase and the effect of mesogenic units. Onsager and Flory [1–2] have treated mesogenic units as rigid cylinders or bars which interact with their neighbours exclusively by their steric demands via repulsive forces. However, in the case of poly(ester-imide)s (PEIs), Krichelodorf [3] has suggested that attractive electronic interactions between mesogenic units play an important role in the stabilization of nematic or smetic order. The optimization of such interactions between π-electrons and dipoles required a stacking of nearly coplanar mesogens. When two imide units were brought together from a great distance, a minimization of the total energy takes place and both imide units formed a stack in copolanar position [4]. These computer simulation results improve a proper understanding of the mesogeneity of imide moieties. However, further experimental support is required. Krichelodorf [5] prepared a kind of LC-PEIs derived from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and di-p-aminophenyl ether of dicarboxylic acids. It has been found that the coplanarity seemed play an important role in stabilizing the mesophase. Hasegawa and Sidorovich [6,7] have found that (trimellitic acid anhydride) phenyl ester had high electronic deficiency because of the para-aromatic ester linkages. The para-aromatic ester linkages could contribute to the formation of self-ordering and favor for the in-plane orientation because of its conformation and polarity. To the best of our knowledge, LC-PEIs prepared via two-step method and forming LC-phase by combining two symmetrical imide mesogenic units has rarely been reported. Therefore, four novel coPEIs were synthesized via two-step method in order to investigate whether two imide mesogenic units which have different conformation and polarity could control the formation and stabilization of LC-phase.

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1. Experimental

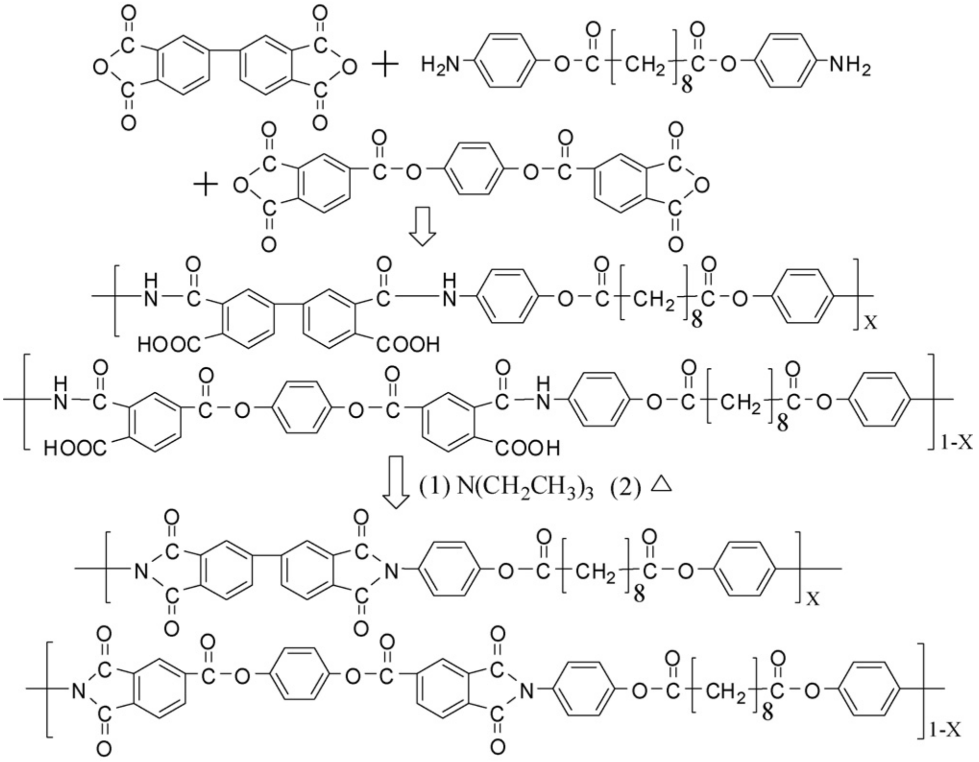
3,3′,4,4′-biphenyltetracarboxylic dianhydride was obtained from Mitsubishi Chemicals and used after drying at 180 °C under vacuum for 5 h. N-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation over phosphorus pentoxide and stored over 4 Å molecular sieves. Tertiary amine (TEA) (from ACROS OGANICS) was used as received.

Bis(trimellitic acid anhydride) phenyl ester (BTAH), m.p.: 277 °C. IR (KBr cm^{-1}): 1842, 1782 °C1741 cm^{-1} (vs, C=O), 1293, 1266, 1228 (C=O). ^{1}H NMR (DMSO-d_6, δ ppm): 8.66(d, 2H, ArH), 8.63(s, 2H, ArH), 8.30(d, 2H, ArH), 7.53(s, 2H, ArH). Di-p-aminophenyl ester of dicarboxylic acids (DAED). m.p.: 112 °C. IR (KBr cm^{-1}): 3202, 3390 (NH_2), 1745 (C=O). ^{1}H NMR (DMSO-d_6, δ ppm): 6.53 (d, 4H, ArH), 6.73 (d, 4H, ArH), 5.11(s, 4H, $–NH_2$,), 3.31(s, 4H, $–COO–CH_2–$), 1.60(s, 4H, $–COO–C–CH_2–$), 1.15(s, 8H, $–CH_2–CH_2–$).

0.02 mmol DAED and 10 mL NMP were added into a 25 mL three-necked flask equipped with a nitrogen inlet and a mechanical stirrer. Once the DAED was fully dissolved, 0.0143 mmol BPDA was added firstly, and then 0.0061 mmol BTAH was added. The reaction mixture was stirred at 5 °C for 5 h under nitrogen, and an appropriate amount of TEA was added to form copoly(ester-amic acid) salt (coPEAAS). Four coPEIs were fabricated by thermal imidization at 300 °C from these coPEAAS.

2. Results and discussion

For the two-step method, hydrolysis reaction would happen in coPEAA chains and cause the chain scission because of the carboxylic group. It has been reported that poly(amic acid) salt (PAAS) are significantly more stable toward hydrolysis as compared to respective PAA [8–9]. The formation of coPEAAS by neutralizing the carboxylic group with TEA was also applied to prevent the hydrolysis of coPEAA. High molecular weight coPEAAS was obtained. The synthetic route of coPEIs is depicted in Scheme 1. Characteristics and relevant data are summarized in Table 1.



Scheme 1. Synthesis of copoly(ester-imide)s.

Table 1
Properties of four copoly(ester-imide)s.

Polymer	BTAH (mol %)	η(dL/g)[a]	T_m(°C)[b]	T_i(°C)[b]	Degree of Crystallinity(%)[c]
A	10	1.47	370	391	38.8
B	20	1.56	355	410	28.4
C	30	1.85	352	412	26.6
D	40	2.03	349	416	25.3

[a] 0.5 g/dL of corresponding coPEAAS in NMP at 25 °C.

[b] T_m and T_i obtained from DSC measurements with a heating rate of 10 °C min^{-1}.

[c] Degree of crystallinity obtained from Philips X'Pert highScore.

After thermal imidization, the characteristic peaks of coPEAAS (1657 and 1556 cm^{-1}) almost disappeared and four characteristic imide bands at 1757, 1711, 1381 and 724 cm^{-1} appeared. The bands at 1381 cm^{-1} and 724 cm^{-1} were the imide carbon-nitrogen stretching and the bending of the imide ring. So these coPEAAS were completely converted into coPEIs by thermal imidization.

With increasing content of BTAH units, the number of diffraction peaks and degree of crystallinity decreased (Fig. 1). Polymer A formed higher order crystal structure than polymer B, C and D. The decrease of the degree of crystallinity could attribute to the disrupting order of the BTAH units.

Two kinds of endothermic transitions temperatures can be observed (Fig. 2). When the content of BTAH units rose from 10% to 40%, the melting temperatures decreased from 370 °C to 349 °C. This fact is consistent with the above WAXD results. However, the isotropization temperatures (T_i) of four coPEIs increased from 391 °C to 416 °C. It has been reported that the interaction and rigidity of molecular chains would be the decisive factor for the change of the T_i

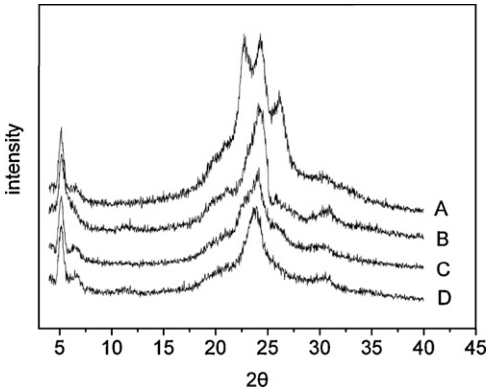


Fig. 1. WAXD powder patterns of four coPEIs.

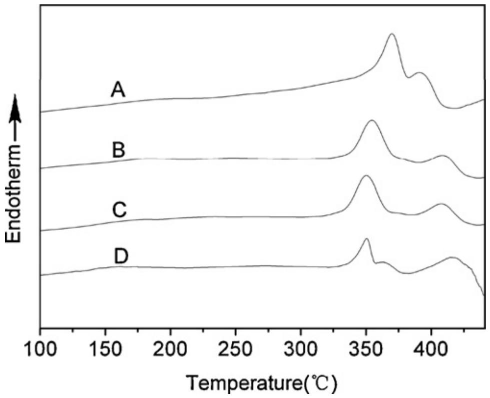


Fig. 2. DSC heating curves of four coPEIs.

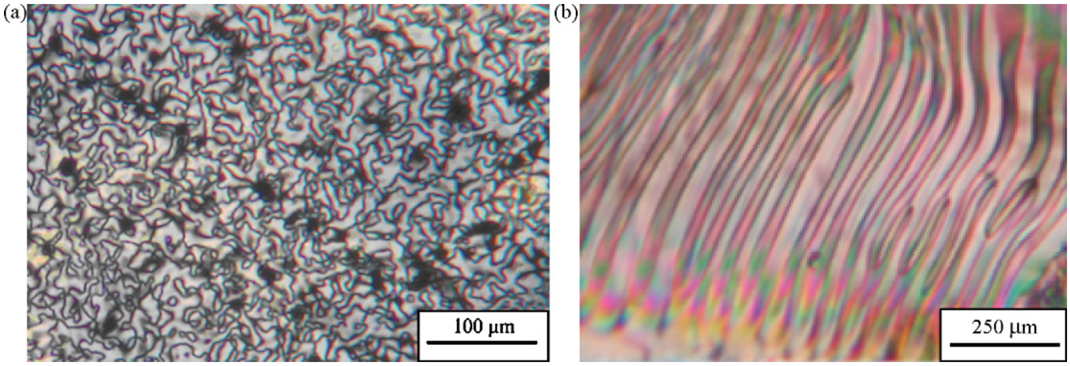


Fig. 3. Polarized light micrographs of textures quenched from mesophases by liquid nitrogen: (a) polymer A, B and D and (b) polymer C.

because the molecular chains in the liquid crystal phase possessed high mobility [10]. The flexibility of BTAH units was higher than that of BPDA units. The electronic deficiency of BTAH units was higher than that of BPDA units because of the polarizability of para-aromatic ester linkages. So the electronic interactions (donor–accepter interactions) of BTAH units were the decisive factor for the increase of T_i.

Kricheldorf [11] has reported that BPDA/DAED homopolymer could form a broad smetic crystalline. However, for polymer A, B and D, nematic phase with typical ‘‘thread schlieren texture’’ was observed (Fig. 3). Polymer C formed the ‘‘Inversion walls texture’’ which fitted with the published nematic phase textures [12,13]. The introduction of BTAH mesogenic units could control the formation of LC-phase.

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