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Original Research Article

Alternating copolyoxamide with high heat resistance and excellent crystallization property via direct solid-state polymerization

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Abstract: Alternating copolyoxamides are of high interest in high-heat-resistant polyamilies owing to their regular molecular chains, high amide group density, and high intermolecular hydrogen bonds. To cope with the high melt condensation temperature, easy thermal degradation and side reactions, as well as the problem of chain structure regularity in traditional methods, we developed a direct solid-state polymerization approach to prepare alternating copolyoxamide from an equimolar diamine-oxalate precursor. At low melting temperatures and high thermal decomposition temperatures, the ordered form of the precursor is converted into a regular polymer chain structure. The structural formation, thermal stability, and crystallinity of the material were analyzed using FTIR, NMR, DSC, TGA, and XRD. Our results show that direct solid-state polymerization promotes oxalamide bond formation, reduces structural defects in high-temperature polymerization, and produces alternating copolyoxamides with a high melting temperature, high thermal decomposition temperature, and distinct crystallization peaks. We demonstrate that the alternating sequence and oxalammium hydrogen bond network lead to high heat resistance and crystallinity of a material, which can be used to create high-end engineering plastics, electronic packaging materials, and heat-deficient fiber materials.
Keywords: alternating copolyoxamide; direct solid-state polymerization; high heat resistance; crystallization properties; polyamide

1. Introduction

Polyamide has been widely used in automotive, electronics, fiber, and structural components owing to its low mechanical properties, wear resistance, chemical stability, and processing flexibility. As materials with high-end equipment and electronic packaging become lighter, heat-resistant, and highly stable, ordinary aliphatic polyamides have been found to be unable to attain the heat distortion temperature, crystallization rate, and long-term service stability. In recent years, the structural design of high-heat-resistant polyamides, copolyoxamide, and bio-based polyamides has been studied. Among them, improving thermal properties and crystallization behavior by increasing regularity of molecular chains and increase hydrogen bonds has proved to be a relatively efficient material design [1-3]. Oxalide contains strongly coupled amide bonds that can give rise to high-density and highly directional intermolecular hydrogen bonds. Compared with normal long-chain aliphatic polyamides, copolyoxamide materials tend to have stronger inter-chain interactions and higher crystalline region stability [1]. High-heat-resistant polyamide materials are sometimes prepared at polymerization temperatures, melt viscosities, and side reactions. Traditional melt polycondensation is a mature process for high-melting-point or strongly hydrogen-bonded polyamidal materials; however, high temperatures can cause end-group imbalance, chain breakage, color deepening, and relatively small molecular weight growth [2].

Direct solid-state polymerization provides a solution, which usually involves a salt precursor/oligomer, followed by a polycondensation reaction in the solid state. The reaction temperature is below the melting point, which can decrease thermal damage and preserve the spatial order of the precursor [2, 4]. Therefore, we focus on "direct solid state polymerization - alternating copolymer structure - thermal and crystallization properties" to build a preparation and characterization scheme for alternating copolyoxamide.

2. Material preparation and characterization methods

Dermine monomers and oxalate precursors were used in the experiment to prepare diamine-oxalate in

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equimolar amounts. Stoichiometric balance and chain sequence regularity are necessary for polymerization, and solvent polarity, reaction temperature, and drying should be controlled during the salt formation process to ensure that the precursor forms a stable and homogeneous solid salt. The salt precursor was washed, filtered, and vacuum-dried for direct solid-phase polymerization.

Direct solid-state polymerization was carried out in nitrogen, and the reaction was performed using a step-heating method. The polymerization temperature was set such that the precursor could be condensation polymerized, but below the polymer melting temperature to keep the material solid or semi-solid. Nitrogen flow was used to remove small-molecule byproducts and reduce oxidative contamination. Five polymerization temperatures of 220, 235, 250, 265, and 280 °C were used to analyze the effect of temperature on the material properties, with the same hold times and conditions.

3. Results and discussion

3.1. Structural formation analysis

FTIR results indicated that the absorption peaks of amide carbonyl and N-H related absorption peaks were much higher, and the ionic characteristic signals in the salt precursor were weak, indicating that diamine-oxalate had been converted into an oxalamide bond structure under solid-state conditions. In the NMR tests, the signal distribution of adjacent methylene groups in the main chain was relatively small, and no complex groups were identified owing to evident random copolymerization, indicating that the material had a good alternating chain sequence, consistent with the findings that alternating copolyoxamide oxaladine forms a stable hydrogen bond network with a highly regular structure [1]. From the reaction path, solid-state polymerization is not simply about reducing the temperature but rather about exploiting the preorganization effect of reactive groups in the salt precursor to allow the end groups to slowly condense under limited diffusion conditions. Compared with melt condensation, this process decreases the probability of excessive chain segment movement and side reactions and helps maintain the repeating units of the alternating structure of the polymer. Similar solid-state polymerization results indicate that the precursor particle structure, reactor design, and small-molecule diffusion pathway affect the molecular weight growth and thermal properties of the final product [2].

3.2. Thermal stability and crystallization properties

The DSC data showed that the sample crystallized well during cooling. The alternating copolyoxamide can be crystallized using a strong force. The polymerization temperature increased from 220 °C to 280 °C, and the material crystallinity increased, indicating that higher temperatures may promote chain growth and local chain segment rearrangement, although this might not be sufficient for end-group imbalance and thermal decay. Therefore, solid-state polymerization must be balanced between chain growth efficiency and thermal stability [5-7].

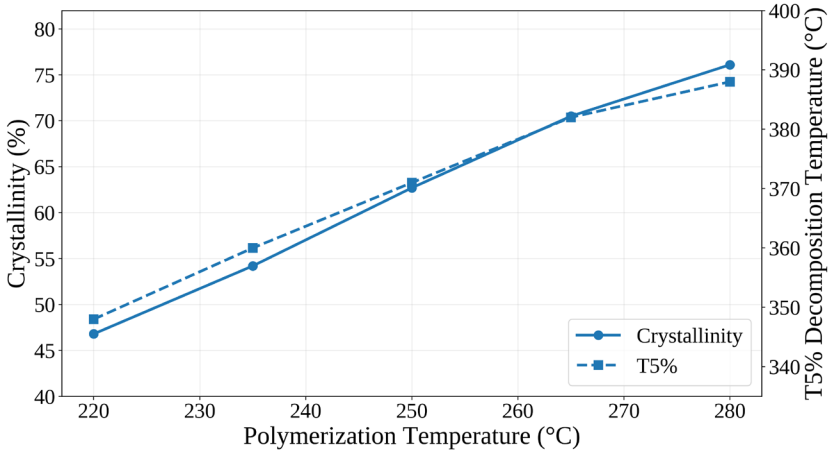

Figure 1. Simulated effects of polymerization temperature on the crystallinity and thermal decomposition temperature.

TGA showed that the 5% thermogravimetric temperature of the sample increased with the polymerization temperature, suggesting that direct solid-state polymerization helps reduce low-molecular-weight residues

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and structural defects. **Figure. 1** illustrates the impact of polymerization temperature on crystallinity and thermal decomposition temperature. The material properties were better after 250 °C, implying that this temperature may be conducive to a stable crystalline region of the oxalamide segments. This pattern follows the conclusion that "chain regularity, hydrogen bonding and thermal history combine to promote crystal formation".

3.3. Structure-performance relationship

The high heat resistance and excellent crystallinity of the alternating copolyoxamide can be explained by two aspects. (1) The oxalamide units increase the number of amide groups, which causes stronger and denser hydrogen bonds between chains; therefore, the energy required for melting the crystal increases. (2) With the alternating copolymer structures, the random chains no longer interfere with the stacking, and it is easier for the repeating units to arrange themselves regularly. The structural regularity of polyamide is usually closely related to the crystallization peak temperature, crystallization rate, and crystal perfection. In addition, direct solid-state polymerization, which also improves performance, is useful. Because the reaction occurs below the melting time, the polymer does not need to remain in a high-viscosity molten state for a long time, leading to high-temperature degradation and side reactions. The ordering of the precursor salt also provides a spatial basis for the alternating segments. Overall, our material properties are not the result of a combination of the precursors, solid-state polymerization temperature, chain segment regularity, and hydrogen bond network.

4. Conclusion

The study considered a highly heat-proof and highly crystalline alternating copolyoxamide and developed a material preparation and performance evaluation system using direct, solid-state polymerization. We showed that an equimolar diamine-oxalate precursor could be used to form an alternating chain structure, and that direct solid-state polymerization facilitated side reactions and thermal degradation at high melting temperatures. FTIR and NMR analyses showed the excellent formation of oxalamide bonds and the alternating structure, while DSC, TGA, and XRD analyses showed that the material was very stable, crystalline, and regular in structure. Overall, the alternating sequence, oxalabrication hydrogen-bond network, and solid-state surface polymerization conditions provided a summary of the full performance of the material. This study offers a feasible technical direction for preparing high-performance polyamide materials and can serve as a reference for heat-resistant engineering plastics and electronic packaging materials.

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