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HAL Authorization

Title : Towards aramid polymers by ring-opening polymerization

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Summary: Aromatic polyamides, also known as aramids, are an important class of high-performance polymers. However, in contrast to nylon polymers, they cannot be produced through ring-opening polymerization. In this issue of Chem, Diaconescu et al. present a novel approach to enable this polymerization process, resulting in the synthesis of unprecedented ortho-aromatic aramids.

Nylon polymers, first developed one hundred years ago, are a class of synthetic materials that have seen widespread use, with an annual production that exceeds 6 million metric tons.¹ The inaugural nylon, designated as nylon 66, was first synthesized through the polycondensation of adipic acid and hexamethylene diamine. This material has been shown to possess a number of advantageous properties, including low thermal conductivity and corrosion resistance, which has led to its widespread adoption in various industrial and commercial applications.² Nylon 6 has a similar structure but is easier to synthesize via ring-opening polymerization (ROP, figure 1) of ϵ -caprolactam. While initial ROP methodologies were characterized by their lack of reproducibility, advancements in anionic ROP during the 1960s resulted in accelerated polymerization and reduced monomer residue. Nylon 6 and 66 were particularly noteworthy for their exceptional strength, resistance to abrasion, and thermal performance. As time progressed, a variety of nylons with varying chain lengths and degrees of complexity were developed. These materials exhibit reduced hydrogen bonding, leading to diminished crystallinity and enhanced chemical resistance.³

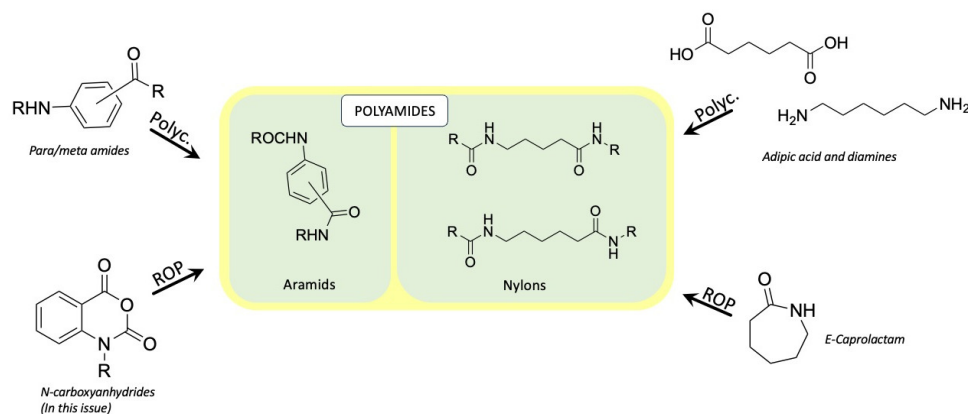


Figure 1. The different ways and key monomers for preparing polyamides. Polyc: polycondensation. ROP: Ring-Opening Polymerization.

A comparison of aromatic polyamides, also known as aramids, and nylon polymers reveals that the former exhibit superior mechanical strength and thermal resistance, characteristics that render them highly suitable for high-performance applications (see Table 1).⁴ These polymers are distinguished by the presence of aromatic rings in their molecular structure, interconnected by amide linkages. The demand for aromatic polyamides is being driven by several factors. These include the increasing adoption of lightweight materials, regulatory pressure for fuel economy, and the need to meet safety standards. However, the manufacturing process of aramid fiber involves a polycondensation step, which imposes limitations on industrial production. This process yields only para- and meta-substituted polyamides, which are characterized by low molecular weight and a significant molecular weight

distribution.⁵ Additionally, the synthesis of ortho-aromatic polyamides has been shown to be a particularly arduous undertaking. In this context, the study proposed by *Diaconescu* et al.⁶ introduces a novel ring-opening polymerization (ROP) technique using N-carboxyanhydrides (NCAs) and transition-metal catalysts to synthesize high-molecular-weight, N-alkylated ortho-aromatic polyamides with tunable properties.

Table 1. Comparison between nylon polymer and aromatic polyamides.

Property	Nylon	Aramids
Flexibility	High	Low (very rigid chains)
Melting temperature	180-260°C	Often above 400°C
Thermal resistance	Moderate	Excellent
Tensile strength	Good	Exceptional
Flame resistance	Poor	Excellent

In the domain of protein-like polymers, ROP of NCA has emerged as the predominant synthetic approach for polypeptide synthesis.⁷ Significant attention was devoted to identifying suitable initiators that could effectively activate NCAs and promote the ROP of polypeptides with the desired degree of polymerization (D_p) and a narrow dispersity (\mathcal{D}) of the molar mass. Subsequent to the pioneering work of *Deming's* group,⁸ which introduced organometallic cobalt- or nickel-based initiators to enhance the synthesis of well-defined polypeptides, a plethora of initiation systems have been identified for the living polymerization of NCAs. These include organosilicon, Lewis pairs, amine, and ammonium salt. The employment of catalysts has emerged as a pivotal strategy to enhance the initiation and propagation stages of polymerization. This encompasses the employment of metallic and organocatalysts. Despite the extensive investigation of metallic catalysts in polymer chemistry, the discovery of metallic catalysts for NCA ROP is rarely reported, possibly due to the difficulty in selecting the appropriate pairs of metals and ligands. It is in this context that the study proposed by *Diaconescu* et al. introduces developed a transition-metal catalyzed ROP method utilizing Schiff base metal complexes (e.g., aluminum, cobalt, chromium), a cocatalyst ([PPN]Cl), and propylene oxide (PO) to activate aromatic 6-membered-ring NCAs (6-NCA-R). This approach enables a chain-growth polymerization process, yielding polyamides with higher molecular weights and narrower dispersities than traditional polycondensation routes. Beta-NCAs are theoretically useful precursors to poly(beta-peptides).⁹ Beta-NCAs are readily synthesized either by phosgenation of free beta-amino acids (Fuchs-Farthing method) or through the cyclization of urethane-protected amino acids (Leuchs method). This was rather recently achieved by *Diaconescu* et al by simply using CO₂.¹⁰

In the work developed in this issue of Chem,⁶ initial experiments showed that common aromatic primary amines failed to initiate polymerization of 6-NCA-R due to its low reactivity. The research team screened various metal complexes—especially those based on ferrocene, cobalt, chromium, and manganese. Among them, (salph)AlCl (Al-2) emerged as the most effective, demonstrating superior yield, molecular weight control, and initiation efficiency. The combination of Al-2 and [PPN]Cl, with PO as a co-solvent and initiator, was found to be essential. Without any one of these components, polymerization did not occur or was poorly controlled. The proposed mechanism involves the formation of an aluminum monoalkoxide intermediate via the ring opening of PO. This intermediate initiates the NCA polymerization through decarboxylation, generating a growing polymer chain. Simultaneously, the released CO₂ reacts with PO to form propylene carbonate, effectively removing the by-product and driving the reaction forward. MALDI-TOF mass spectrometry confirmed the presence of alkoxide end groups in the polymer chains, supporting the proposed initiation pathway. The authors investigated how variations in cocatalyst concentration, PO equivalents, solvent choice, and temperature influenced polymerization. Neat PO was identified as the optimal medium due to its dual role as both solvent and CO₂ scavenger. Polymerizations conducted in THF or cyclohexene oxide (CHO) were less efficient or

required extended times. Higher monomer feed ratios produced polymers with greater molecular weights, and initiation efficiencies improved at elevated monomer concentrations, indicating a well-controlled living polymerization. The system's versatility was showcased through successful block copolymerizations of different NCAs and one-pot copolymerizations with cyclic anhydrides (e.g., phthalic anhydride, phthalic thioanhydride). These reactions yielded copolymers with tailored properties. Sequential block copolymerizations resulted in monomodal molecular weight distributions, indicating a clean chain extension. Diffusion-ordered spectroscopy (DOSY) confirmed block structures. Although some copolymers displayed multimodal distributions due to differing monomer reactivity, the overall success demonstrated the system's robustness. The resulting polymers exhibited high thermal stability and differential scanning calorimetry (DSC) revealed that the melting temperatures (T_m) and glass transition temperatures (T_g) were influenced by the side-chain length. Polymers with longer *N*-alkyl chains (e.g., octyl) were more soluble in common organic solvents like THF and DCM. Interestingly, even short side chains (ethyl) conferred sufficient solubility, placing ortho-polyamides' behavior between their para and meta counterparts.

Overall, the work proposed by *Diaconescu et al.* establishes a novel synthetic route to high-performance ortho-aromatic polyamides via metal-catalyzed ring-opening polymerization of 6-NCA-R monomers. It offers unprecedented control over polymer architecture, molecular weight, dispersity, and physical properties. The method allows incorporation of functional side chains and heteroatoms, paving the way for advanced materials in electronics, coatings, and structural composites. The insights gained also enrich the understanding of ring-opening polymerizations involving less-reactive monomers and complex catalytic systems.

References

1. <https://www.vantagemarketresearch.com/industry-report/nylon6-and-nylon66-market-3684>.
2. P. Matthies and W. F. Seydl, in *High Performance Polymers: Their Origin and Development*, ed. R. B. Seymour and G. S. Kirshenbaum, Springer Netherlands, Dordrecht, 1986, pp. 39–53
3. M. Varghese, M. W. Grinstaff, *Chem. Soc. Rev.*, 2022, 51, 8258-8275.
4. B. Yang, L. Wang, M. Zhang, J. Luo, Z. Lu, X. Ding, *Adv. Funct. Mater.*, 2020, 30, 2000186.
5. J.A.R. Reglero Ruiz, M. Trigo-Lopez, F.C. Garcia, J. M. Garcia, *Polymers*, 2017, 9, 44–414.
6. Deng et al., 2025, *Chem* 11, 1–13. <https://doi.org/10.1016/j.chempr.2024.12.004>.
7. Y. Wu, K. Chen, J. Wang, M. Chen, W. Dai, R. Liu, *J. Am. Chem. Soc.*, 2024, 146 (35), 24189-24208.
8. T.J. Deming, *Nature*, 1997, 390 (6658), 386-389.
9. J. Cheng, J.W. Ziller, T. J. Deming, *Org. Lett.*, 2000, 2, 13, 1943-1946.
10. T.V. Tran, Y. Shen, H.D. Nguyen, S. Deng, H. Roshandel, M.M. Cooper, J.R. Watson, J.A. Byers, P.L. Diaconescu, L.H. Do, *Green Chem.*, 2022, 24, 9245-9252.