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Reactive Macrocyclic Ether−Urethane Carbodiimide (MC−CDI): Synthesis, Reaction, and Ring-Opening Polymerization (ROP)

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Introduction. Cyclic oligomers characterized by lower melt viscosities than their linear counterparts have shown to be excellent for synthesizing step-growth thermoplastics. Successful examples include syntheses of polycarbonate, poly(ether ketone), poly(ether sulfone), poly(ether−sulfide), aryl polyamide, poly(ether−imide), and polyester.[1−4] In all these cases, appropriate initiators start the entropy-driven ring-opening polymerization (ROP) of the macrocyclic polymer intermediates to achieve macromolecules. However, these reactive ROP processes are carried out at a high temperature in excess of over 200 °C. For practical and energy considerations, development of lower activating temperature cyclic intermediates, in which heat-labile linkages are built into the system will be highly desirable for ROP process.

In our recent study, we recognized aryl carbodiimide (CDI) as a versatile functional group[5] that may be a possible candidate fitting a lower temperature ROP process. Aryl carbodiimide (CDI) can be prepared directly from any aromatic isocyanates.[6] The acid adduct, *N*-acylurea, formed readily by mixing CDI and carboxylic acids at ambient temperature, can be thermally rearranged to amide and highly reactive isocyanate (NCO) at above 120 °C in the absence of catalyst.[5] Introduction of *N*-acylurea groups into a macrocyclic ring via CDI linkage would facilitate self-ring-opening of cyclic intermediates at reasonably low activation temperatures of 100 to 150 °C.

Furthermore, we have developed a sequential self-repetitive reaction process ("SSRR") to prepare poly(amide−imide) from acid-ester functionalized polyacylurea.[5] The "SSRR" process involves a series of repetitive reactions including (i) thermal rearrangement of *N*-acylurea to form amide and isocyanate; (ii) condensation of isocyanate into CDI in the presence of a CDI catalyst; and (iii) addition of more acid to the CDI to yield a new *N*-acylurea. In this process, all CDIs, acids and isocyanates were exhausted at the end of the reaction cycle and all amides or polyamides reacted to completion fully forming into the final products. In this communication, we are reporting the preparation via our developed sequential self-repetitive reaction ("SSRR") of a reactive macrocyclic ether−urethane carbodiimide (MC-CDI) which is the key starting intermediate for synthesizing poly(amide−urethane) and poly(amide−imide−urethane).

Results and Discussion. MC-CDIs were prepared by an intramolecular end-to-end ring-closure process[7−10] using isocyanate-terminated prepolymers based on toluene 2,4-diisocyanate (2,4-TDI). These TDI-prepolymers (T2Pm; Scheme 1) were prepared according to Bartelink's method by treating 2,4-TDI with four different poly(propylene glycol) (PPG) diols with molecular weights (*m*) of 192, 400, 700, and 2000 individually.[11] All the cyclizations of prepolymers were then run at 90 °C under high dilution of 0.013M in toluene and in the presence of 1,3-dimethyl-3-phospholene oxide (DMPO) (Scheme 1). The cyclic CDI group was made by linking the terminal isocyanate groups intramolecularly with evolution of CO_2.

Table 1. Yield and Properties of Isolated MC-CDI

sample	cyclization yield (%)[a]	T_g of soft segment (°C)	melting point (°C)
MC-CDI-T2P192	60	18.0 (110.0[b])	80.5−85.2[c]
MC-CDI-T2P400	67	6.7	16.0 and 22.0[d]
MC-CDI-T2P700	40	3.8	N/A
MC-CDI-T2P2000	18	−49.0	N/A

[a] Isolated by column chromatography. [b] T_g of hard segment. [c] Measured by melting-point apparatus (3 °C/min). [d] From the second heating thermogram of DSC (10 °C/min).

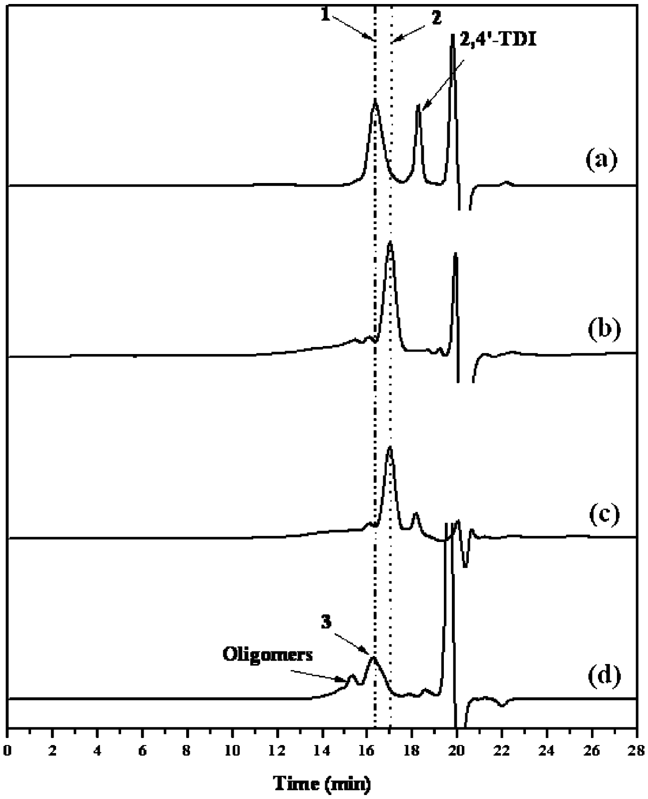

Figure 1. GPC chromatograms of NCO-terminated prepolymer T2P700 (a), MC-CDI-T2P700 (b), MC-ACU-T2P700-AcA (c), and its ring-opened linear product L-AU-T2P700 (d).

Under high dilution, the reaction yields the targeted MC-CDIs which bear single CDI linkages, as their main components. However, the GPC analysis indicates that crude cyclization products contained a mixture of multiple molecule weight and CDI-containing cyclic products, rather than one single product. Since, the crude MC-CDI was found to be stable in water at neutral conditions, this allows us to purify the crude mixtures by column chromatography (solid phase, silica gel; eluent, ethyl acetate) and isolate the target products for structure characterizations. The isolated yields of these target MC-CDIs ranged from 20 to 70%, with percentages higher for smaller ring sizes (Table 1). Consistent to previous literature observations,[9] all of the isolated MC-CDIs showed a major peak with a slightly higher retention time than those of their respective linear counterparts (Figure 1).

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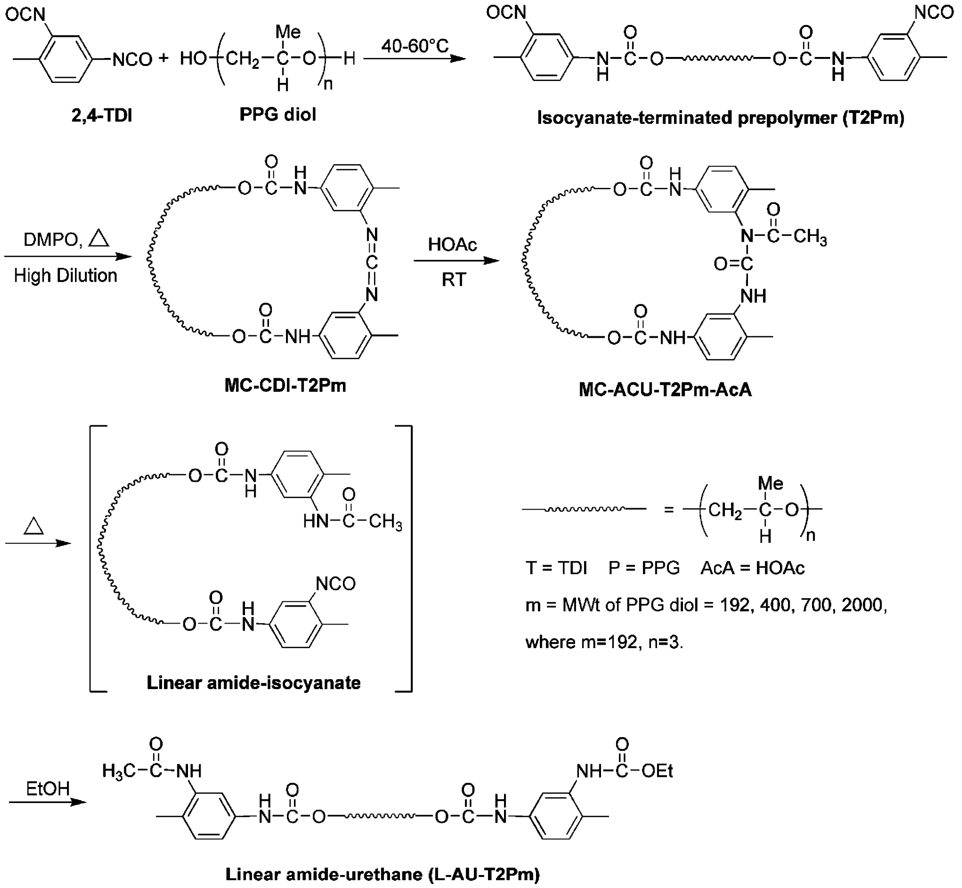
Scheme 1. Syntheses of MC−CDI and MC-ACU and Self-Ring-Opening Model Reaction



Also concurring with reported phenomena,[8−10] the thermal behaviors exhibited in DSC show an increase of PPG soft segment T_g(s), as ring size decreases. (Table 1) This observation suggests that with decreasing ring size, torsion mobility of polyether segments gradually becomes constrained. Moreover, it is interesting to point out that the smallest ring system, MC-CDI-T2P192 (Scheme 1; derived from two TDIs and one PPG-192), turns unexpectedly into a crystalline product with its mp at 85 °C. Therefore, MC-CDI-T2P192 was purified by recrystallization and complete structural characterizations were performed by ^{13}C NMR, elemental analysis, and FAB mass spectrum. These analyses firmly established that its structure possesses only one single CDI-linkage.

Because aromatic CDI can react with carboxylic acid to form *N*-acylurea in high yields,[5] the purified MC-CDI-T2P700 (Scheme 1; derived from two TDIs and one PPG-700) was selected for our functionalization in its macrocyclic ring at CDI linkage. As shown in Scheme 1, the reaction of acetic acid (AcA) and MC-CDI-T2P700 was carried out in toluene at room temperature, and the isolated yield of the acylurea, MC-ACU-T2P700-AcA, was essentially quantitative. The purified MC-ACU-T2P700-AcA showed a higher retention time in GPC than that of the linear precursor, T2P700 (shown in Figure 1c). This implies that the acylurea formation retains its ring structure. When the ringed acylurea was then subjected to heat at 120 °C in xylenes, the cyclic *N*-acylurea was thermally rearranged to a linear amide−isocyanate as evidenced by the formation of a 2270 cm^{-1} NCO-absorption in IR (Figure 2). The GPC of the product quenched with ethanol also showed a decrease in retention time consistent with those of linear prepolymers (Figure 1). The GPC analysis proves the MC-ACU became reactive upon heating and underwent a ring-opening reaction to form new reactive amide−isocyanate groups.

We have applied this ring-opening reaction to prepare poly(amide−urethane) (PAU) from acid-functionalized MC-ACU-T2P700-AdA (Scheme 2) and poly(amide−imide−urethane) (PAIU) from acid-ester functionalized MC-ACU-T2P700-TAE (Support information, Scheme S1). The first acylurea polymer intermediate was prepared by reacting MC-CDI-T2P700 with adipic acid (AdA) in toluene/THF at room temperature. MC-ACU-T2P700-AdA, was isolated in yield of 98%. When the polymer intermediate was heated to 105−120 °C in DMF solution, the *N*-acylurea group on the ring smoothly generated an open-chained product with an isocyanate group on one end and a carboxylic group on another, as indicated in Scheme 2. By following the “SSRR” reaction sequence[5] under the aid of DMPO at 120 °C, high molecular weight PAU was obtained.

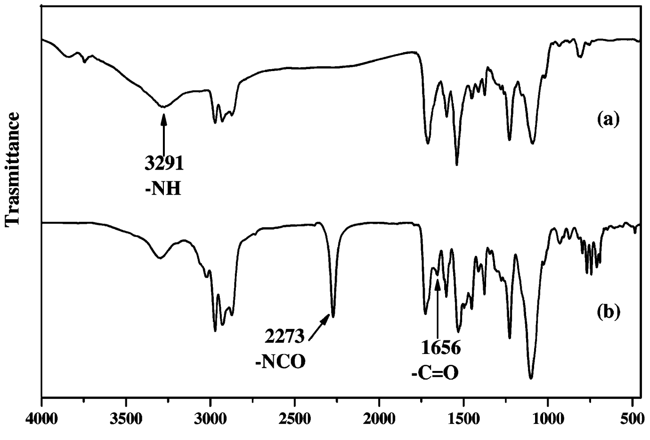


Figure 2. IR monitoring of ring-opening reaction at 130 °C: (a) original MC-ACU-T2P700-AcA; (b) ring-opened MC-ACU-T2P700-AcA.

Scheme 2. Synthesis of Acid-Functionalized MC−Acylurea and Its Ring-Opening Polymerization to Yield Poly(amide−urethane)

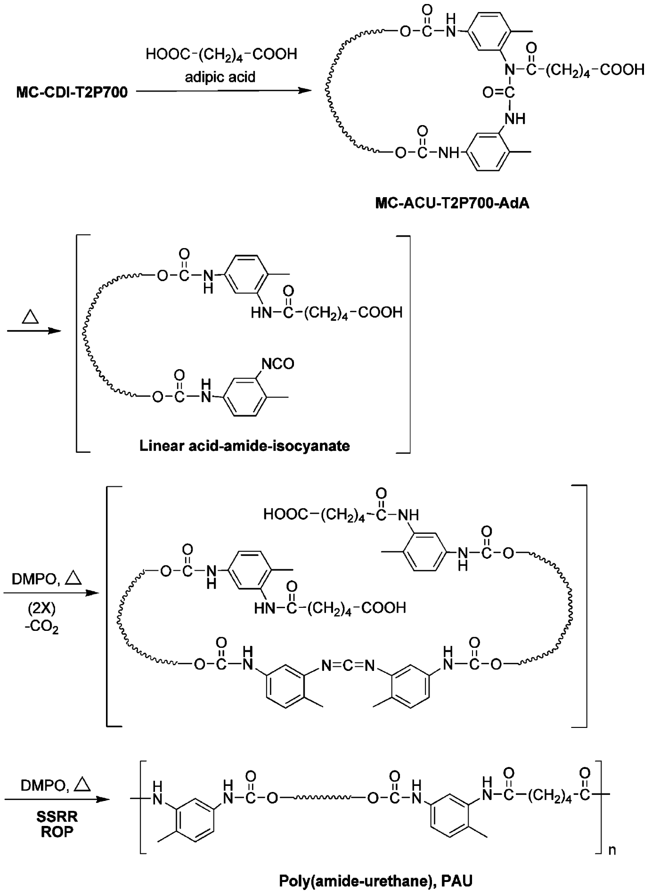


Table 2. The GPC Analysis of ROP Products[a]

sample	M_w[b]	M_w/M_n[b]	area (%)
poly(amide−urethane)	94 721	1.894	100
poly(amide−imide−urethane)	759 084	1.620	61
	44 071	1.233	39

[a] DMF as eluent at flow rate of 1.0 mL/min. [b] Corresponding to PS standards.

The final PAU was isolated in 86% yield by precipitation of its DMF solution in toluene, and was characterized to have a soft segment T_g at −43 °C, a hard segment T_g at 147 °C by DSC and T_d (5% weight loss) at 289 °C by TGA. Similarly, PAIU was also synthesized through SSRR-based ROP of ortho-acid-ester functionalized MC−acylurea intermediate (MC-ACU-T2P700-TAE), which was made from MC-CDI-T2P700 and trimellitic anhydride (TMA) and followed by alcoholysis of the cyclic anhydride. The GPC analysis in Table 2 shows that the overall ROP processes produced high molecular weight polymers in both cases.

In summary, we have synthesized a series of new aromatic MC-CDIs and isolated the pure MC-CDIs possessing only one CDI linkage. The model reaction of the purified MC-CDI-T2P700 with acetic acid produces cyclic acylurea (MC-ACU-T2P700-AcA), which can undergo a ring-opening reaction at above 120 °C with formation of a linear amide−isocyanate intermediate. Most significantly, these novel reactive macrocyclic intermediates could undergo self-ring-opening and the subsequent one-step polymerization in solution at around 120 °C to form modified polyurethanes of high molecular weight. Thus, the macrocyclic acylureas are, in essence, a new latent isocyanate system and can be activated under mild conditions. This ring system seems ideal for devising a one-component urethane system or self-curing systems without the presence of toxic isocyanate group in the formulation. Further exploration of this technique is being conducted and will be reported in the near future.

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Supporting Information Available: Text giving experimental procedures, a scheme showing the synthesis of the acylurea and its polymerization, figures showing IR spectra, ^{1}H NMR spectra, GPC chromatograms, mass spectra, ^{13}C NMR spectra, and DSC and TGA thermal analysis for the corresponding compounds, and tables of reaction conditions and elemental analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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