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High-Pressure Synthesis of New Aromatic Poly(diazetidinediones) by Cyclodimerization Polymerization of Aromatic Diisocyanates

Kazuo Itoya, Masa-aki Kakimoto, and Yoshio Imai*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

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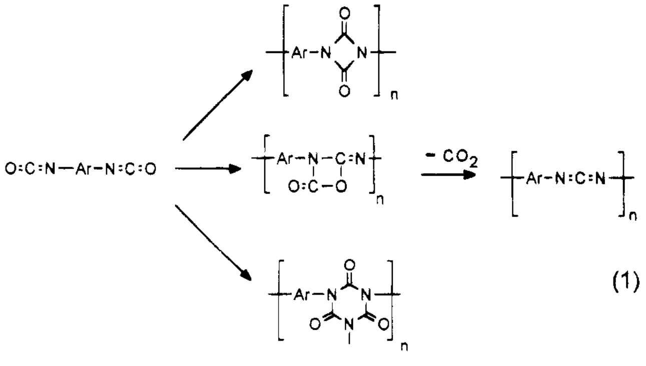
ABSTRACT: New aromatic poly(diazetidinediones) having a strained four-membered heterocyclic ring structure, which we were unable to obtain by the polymerization under atmospheric pressure, were synthesized for the first time by the cyclodimerization polymerization of aromatic diisocyanates under high pressure without use of solvent or catalyst. As shown by a model compound study, aromatic monoisocyanates cyclodimerized almost quantitatively, yielding 1,3-disubstituted 1,3-diazetidine-2,4-diones at 180–200 °C under 400–800 MPa for 20–40 h. Aromatic diisocyanates were converted cleanly to poly(diazetidinediones) through the cyclodimerization polymerization at 200 °C under 700 MPa for 20 h. The polymers formed were pale yellow, opaque, hard solids with high crystallinity and insoluble in any solvent. They depolymerize drastically at around 270 °C in nitrogen into the parent diisocyanates.

Introduction

Aromatic and aliphatic diisocyanates are widely used as monomers for preparing polymers such as polyurethanes and polyureas.[1,2] Aromatic diisocyanates alone can also form linear polymers having a strained four-membered 1,3-diazetidine-2,4-dione ring structure or carbodiimide connecting group and cross-linked polymers with a stable six-membered isocyanurate ring (1,3,5-trisubstituted hexahydro-*s*-triazinetrione) under certain reaction conditions (eq 1).[1-3]



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In fact, the synthesis of polycarbodiimides from aromatic diisocyanates has been known since the early 1960s,[4,5] and cross-linked polymers having an isocyanurate structure from aromatic diisocyanates are also known for applications in the development of high-temperature polymers or the modification of polyurethanes.[6,7] However, the synthesis and properties of aromatic poly(diazetidinediones) having a well-defined structure were relatively unknown for many years. The lack of information on poly(diazetidinediones) prompted us to investigate this type of heterocyclic polymer.

The application of high pressure to facilitate cycloaddition reactions has been demonstrated to be extremely effective for both kinetic and thermodynamic reasons.[8,9] Reports have been published on the cyclodimerization and cyclotrimerization of aromatic isocyanates; phenyl isocyanate cyclodimerized when heated under pressure without a solvent or catalyst,[10] and cyclotrimerization of the isocyanate was accelerated in the presence of triethylamine under high pressure.[11] We have found that the cyclodimerization polymerization of aromatic diisocyanates takes place under high pressure without use of either solvent or catalyst, readily affording the polymers having a well-defined diazetidinedione structure. Poly(diazetidinediones) could not be obtained by the polymerization under atmospheric pressure. This paper is the third in our series on the high-pressure cycloaddition polymerization[12,13] and deals with a successful synthesis of new poly(diazetidinediones) from aromatic diisocyanates and their properties (eq 2).

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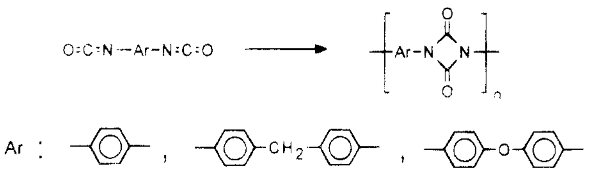

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Experimental Section

Apparatus. The high-pressure reaction was carried out by using a piston–cylinder type hot-pressing apparatus described previously.[12]

Materials. Aromatic monoisocyanates and diisocyanates such as phenyl isocyanate (PI), *m*-tolyl isocyanate (MTI), *p*-tolyl isocyanate (PTI), *p*-chlorophenyl isocyanate (CPI), 2,4-tolylene diisocyanate (TDI), and 4,4′-methylenebis(phenyl isocyanate) (MDI) were obtained commercially. Other diisocyanates, *p*-phenylene diisocyanate (PDI) and 4,4′-oxybis(phenyl isocyanate) (ODI), were supplied by Tonen Petrochemical Co., Japan. All the mono- and diisocyanates were purified by vacuum distillation.

High-Pressure Cyclodimerization of Aromatic Isocyanates. A typical example is given below. A 0.50-g portion of phenyl isocyanate was placed in a Teflon capsule (10 mm inside diameter), and then the capsule was loaded into the cylinder. The piston–cylinder was set at the furnace, and the pressure was applied by a hydraulic press at room temperature to the monomer, followed by increasing temperature. The reaction was carried out at different temperatures between 120 and 200 °C under a pressure of 250–780 MPa for 3–40 h. The reaction temperature was recorded from the point where the temperature was reached to the prescribed one, which usually required 1 h. After the reaction, the temperature was lowered to room temperature, followed by releasing the pressure to 1 atm. The product, 1,3-diphenyl-1,3-diazetidine-2,4-dione, was isolated by washing with toluene, and the resulting white solid was filtered and dried. Mp: 195 °C (by DTA at a heating rate of 10 °C·min^{-1}; lit.[14] mp 175 °C). IR (KBr): 1780 cm^{-1} (C=O).

High-Pressure Synthesis of Aromatic Poly(diazetidinediones). Polymer from MDA. A Teflon capsule (10 mm inside diameter) was used for the polymerization of MDI (0.50 g). The polymerization was carried out at different temperatures between 120 and 200 °C under a pressure of 150–700 MPa for 5–40 h, giving aromatic poly(diazetinedione). After the reaction, the polymer in the form of a flat cylindrical pellet (10 mm diameter and 2–3 mm thick) was removed from the Teflon capsule, followed by washing with toluene and drying. IR (KBr): 1774 cm^{-1} (C=O). Anal. Calcd for $(C_{15}H_{10}N_2O_2)_n$: C, 71.99; H, 4.03; N, 11.19. Found: C, 72.22; H, 3.67; N, 11.38.

The other poly(diazetidinediones) from PDI and ODI were synthesized by the same procedure as that described above.

High-Pressure Synthesis of Cyclodimer from TDI. A 0.50-g portion of TDI was placed in a Teflon capsule, and the reaction was conducted at 250 °C under 650 MPa for 40 h. The product was isolated by washing with toluene. Yield: 0.48 g (96%). Mp: 161 °C (by DTA; lit.[15] mp 155.4–155.7 °C). IR (KBr): 2270 (N=C=O) and 1770 cm^{-1} (C=O).

Measurements. IR spectra were recorded on a Jasco FT/IR-5000 spectrophotometer. Differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DTA-40 and TGA-40, respectively. Wide-angle X-ray diffraction patterns were obtained by using a Rigakudenki RU-200 diffractometer with nickel-filtered Cu Kα radiation by scintillation counters at 50 kV and 180 mA.

Results and Discussion

High-Pressure Cyclodimerization of Aromatic Isocyanates. It has been shown only briefly that aromatic isocyanates cyclodimerize in the presence of various catalysts, giving 1,3-disubstituted 1,3-diazetidine-2,4-diones (eq 3),[14,16] and even without catalyst under high pressure.[17] However, no detailed studies on the high-pressure cyclodimerization of aromatic isocyanates have been reported. Therefore, we first investigated the cyclodimerization of aromatic isocyanates under high pressure in detail.

The high-pressure cyclodimerization of phenyl isocyanate was carried out in the absence of both solvent and catalyst by using a piston–cylinder type hot-pressing apparatus.[12] Curve B in Figure 1 shows a typical IR spectrum of the cyclodimer, 1,3-diphenyl-1,3-diazetidine-2,4-dione, synthesized at 200 °C under 750 MPa for 20 h. The IR spectrum exhibited strong absorption bands at 1776 and 1753 cm^{-1} due to the presence of the 1,3-diazetidine-2,4-dione ring, with the disappearance of an absorption band at 2280 cm^{-1} characteristic of the isocyanate group (curve A in Figure 1) as well as with the absence of bands at 2130 and 1700 cm^{-1} due to carbodiimide and isocyanurate units, respectively.

Figure 2 shows the effects of reaction temperature and applied pressure on the cyclodimerization of phenyl isocyanate for 40 h. Phenyl isocyanate did not cyclodimerize under atmospheric pressure at 120 °C but cyclodimerized when high pressure was applied. As the applied pressure increased, the yield of the cyclodimer increased, and it shifted to higher values with increasing reaction temperature. Figure 3 shows the effects of reaction temperature and time on the cyclodimerization of phenyl isocyanate under 750 MPa. Longer reaction times gave higher yields of the cyclodimer. These results clearly indicated that the cyclodimerization was accelerated by the application of high pressure. However, when the reaction was carried out at a temperature of 140 °C or below, the yield of the cyclodimer was lower than 40%, and hence a temperature higher than 160 °C was required to complete the cyclodimerization.

Table 1 summarizes the results of high-pressure cyclodimerization of various aromatic isocyanates. These isocyanates cyclodimerized at 180–200 °C under 400–780 MPa to give the corresponding 1,3-disubstituted 1,3-diazetidine-2,4-diones in excellent yields. All the reaction products were identified as the proposed compounds by their IR spectra and melting points.[14] These cyclodimers showed characteristic carbonyl absorption bands at the 1750–1780-cm^{-1} region.

High-Pressure Synthesis of Aromatic Poly(diazetidinediones). The high-yield model reaction was extended to the high-pressure polymerization of aromatic diisocyanates. First, MDI was used as a typical diisocyanate monomer. Under atmospheric pressure, MDI could polymerize at a temperature above 120 °C without any catalyst, giving a yellow, transparent polymer. However, the polymer formed by the polymerization under atmospheric pressure at 200 °C for 15 h was found to have no 1,3-diazetidine-2,4-dione structure but to have both carbodiimide and isocyanurate units as evidenced in the IR spectrum by the appearance of strong absorption bands at 2130 and 1700 cm^{-1}, respectively (curve B in Figure 4).

On the other hand, MDI was converted cleanly to poly(diazetidinedione) through the cyclodimerization polymerization at 120–200 °C under a high pressure of 150–700 MPa for 15–20 h without use of either solvent or catalyst, which was followed by IR spectroscopy by the disappearance of an absorption band at 2284 cm^{-1} characteristic of an isocyanate group and the

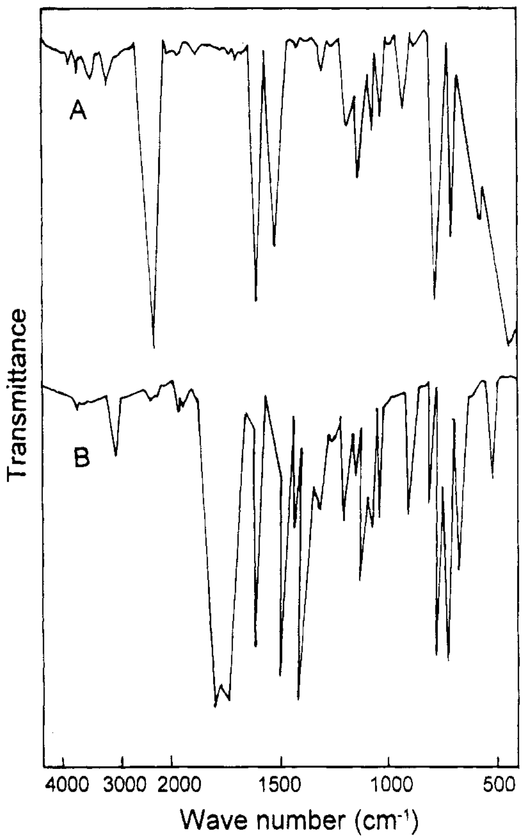


Figure 1. IR spectra of (A) phenyl isocyanate and (B) 1,3-diphenyl-1,3-diazetidine-2,4-dione formed by the cyclodimerization of phenyl isocyanate at 200 °C under 750 MPa for 20 h.

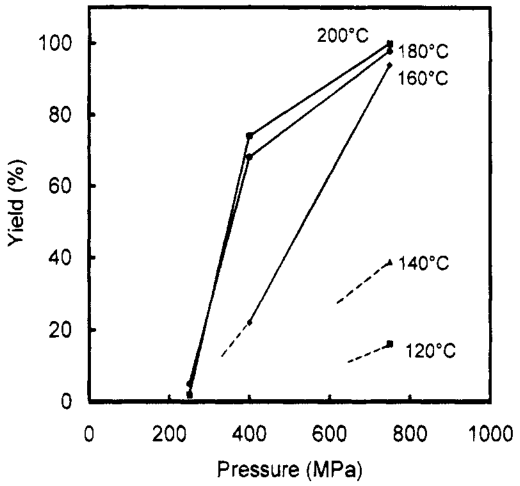


Figure 2. Effects of reaction temperature and applied pressure on the yield of 1,3-diphenyl-1,3-diazetidine-2,4-dione formed by the cyclodimerization of phenyl isocyanate for 40 h.

simultaneous appearance of a new band at 1774 cm^{-1} due to the diazetidinedione ring (curve C in Figure 4).

Figure 5 shows the effects of reaction temperature and applied pressure on the yield of the poly(diazetidinedione) obtained by the polymerization of MDI for 15 h. The yield increased monotonically with increasing reaction temperature, and it shifted to higher values with increasing pressure. The results also indicated that the cyclodimerization polymerization of MDI giving poly(diazetidinedione) was accelerated by the application of high pressure. In addition, this cyclodimerization polymerization probably proceeded in a melt state rather than in a solid state.

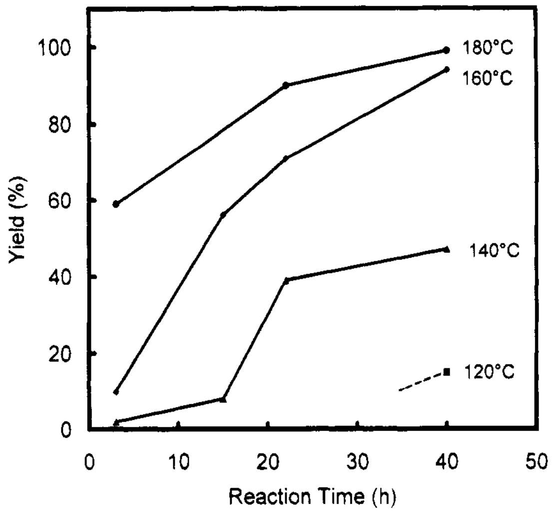


Figure 3. Effects of temperature and time on the yield of 1,3-diphenyl-1,3-diazetidine-2,4-dione formed by the cyclodimerization of phenyl isocyanate under 750 MPa.

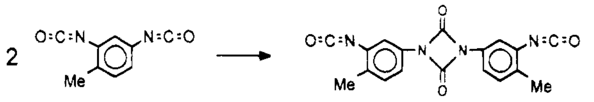
Table 1. High-Pressure Cyclodimerization of Aromatic Isocyanates

	reaction conditions			cyclodimer	
isocyanate	temp, °C	pressure, MPa	time, h	yield, %	mp,[a] °C
PI	140	780	20	39	
PI	200	780	20	99	195 (175)
MTI	160	780	20	0	
MTI	180	780	20	81	192 (185)
PPI	200	400	20	87	166 (160)
CPI	180	780	20	50	
CPI	200	780	40	91	185 (155)

[a] Determined by DTA at a heating rate of 10 °C·min^{-1} in air. The value in parentheses is that reported in the literature.[14]

In addition to MDI, aromatic diisocyanates PDI and ODI were readily converted to poly(diazetidinediones) through the cyclodimerization polymerization at 200 °C under 700 MPa for 20 h. All three polymers formed were pale yellow, opaque, hard solids. The formation of poly(diazetidinediones) by high-pressure cyclodimerization polymerization was confirmed by means of IR spectroscopy and elemental analysis. All the polymers exhibited a new absorption band in the 1770–1780-cm^{-1} region based on the diazetidinedione ring, with the disappearance of a characteristic absorption at around 2280 cm^{-1} due to the isocyanate group. The elemental analysis values of the polymers were in close agreement with the values for the proposed structure.

In the case of the reaction of TDI, this monomer did not polymerize but gave the cyclodimer[15] almost quantitatively owing to steric hindrance of the adjacent methyl group to the isocyanate moiety (eq 4).



(4)

Properties of Aromatic Poly(diazetidinediones). All of the poly(diazetidinediones) obtained from PDI, MDI, and ODI were insoluble in any solvents probably due to their rigid polymer backbone having a ring structure. However, the probable existence of a small extent of contaminated isocyanurate ring structure causing cross-linking in the polymer backbone cannot be ruled out completely.

Figure 6 exhibits the wide-angle X-ray diffraction patterns of three poly(diazetidinediones) from PDI, MDI,

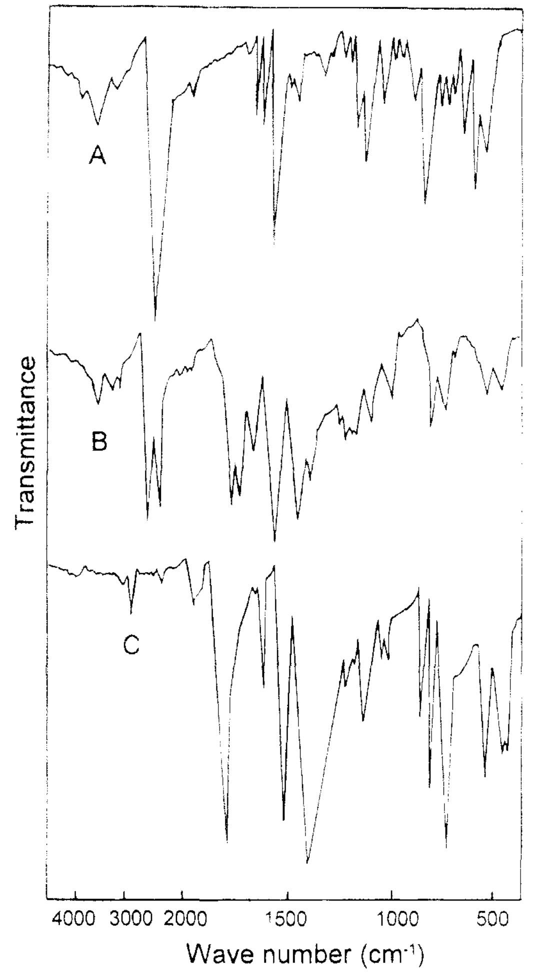


Figure 4. IR spectra of MDI and the polymers of MDI: (A) MDI; (B) the polymer formed by the polymerization of MDI at 200 °C under atmospheric pressure for 20 h; (C) the polymer formed by the polymerization at 200 °C under 750 MPa for 15 h.

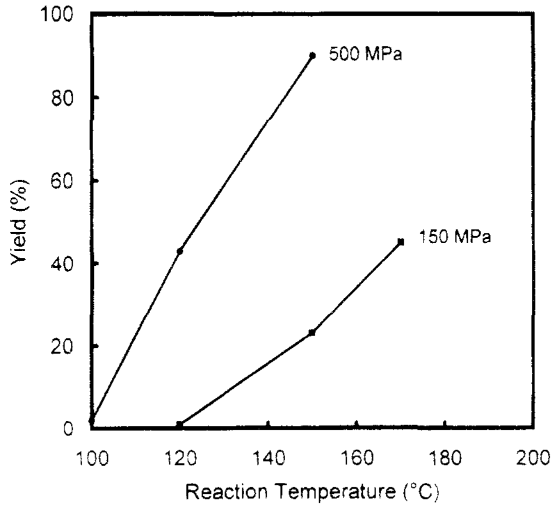


Figure 5. Effects of reaction temperature and applied pressure on the yield of the poly(diazetidinedione) formed by the polymerization of MDI for 15 h.

and ODI. It is obvious that all the polymers were highly crystalline. The high crystallinity might be reflected in part in the insoluble nature of these poly(diazetidinediones).

Figure 7 shows the DTA and TG curves in nitrogen of the poly(diazetidinedione) formed by the polymerization of MDI at 200 °C under 750 MPa for 15 h. This polymer and the other poly(diazetidinediones) began to lose weight at a temperature above 210 °C, followed by drastic weight loss at around 270 °C (TG in nitrogen), giving the parent diisocyanates. The DTA curves also supported the depolymerization of the poly(diazetidinediones). The results of the DTA and TG measurements are summarized in Table 2. Hence, these polymers have some potential for the diisocyanate-generating polymers for the modification of polyurethanes and other diisocyanate-based thermosetting plastics.

When aromatic diisocyanates were subjected to reaction under more severe conditions at a higher temperature of 280–340 °C under high pressure, the cyclotrimerization polymerization occurred, giving the polymers having a cross-linked isocyanurate structure. The high-pressure synthesis of these isocyanurate-

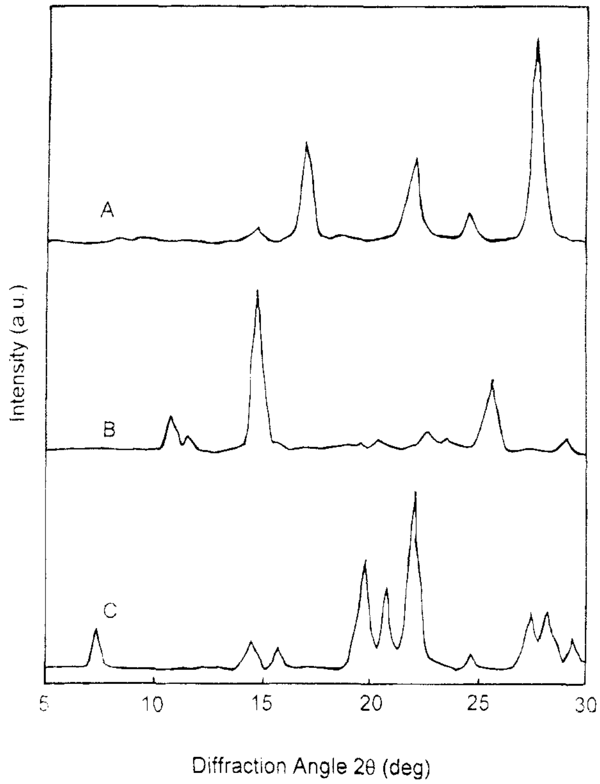


Figure 6. Wide-angle X-ray diffraction patterns of the polymers from (A) PDI, (B) MDI, and (C) ODI formed by the polymerization at 200 °C under 700 MPa for 20 h.

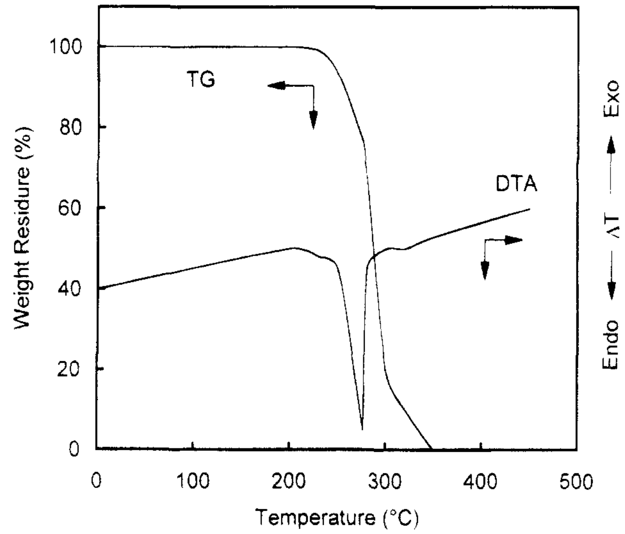


Figure 7. DTA and TG curves of poly(diazetidinedione), formed by the polymerization of MDI at 200 °C under 750 MPa for 15 h, in nitrogen at a heating rate of 10 °C·min^{-1}.

Table 2. Thermal Behavior of Aromatic Poly(diazetidinediones)[a]

	polymer	
diisocyanate	T_d,[b] °C	T_i/T_{10},[c] °C
PDI	276	214/244
MDI	270	217/258
ODI	272	224/256

[a] Obtained by the polymerization of diisocyanates at 200 °C under 700 MPa for 20 h. [b] T_d is the decomposition temperature observed as an endothermic peak temperature by DTA at a heating rate of 10 °C·min^{-1} in air. [c] T_i and T_{10} are initial and 10% weight loss temperatures, respectively, determined by TG at a heating rate of 10 °C·min^{-1} in nitrogen.

containing polymers is the subject of a forthcoming paper.

Conclusions

Phenyl isocyanate, used as the model compound study, cyclodimerized almost quantitatively when the reaction was carried out at 180–200 °C under 400–800 MPa for 20–40 h, giving 1,3-diphenyl-1,3-diazetidine-2,4-dione. Other aromatic isocyanates cyclodimerized in a similar manner. By the extension of the model compound study, aromatic diisocyanates were readily converted to poly(diazetidinediones) through the cyclodimerization polymerization at 200 °C under 700 MPa for 20 h. Thus, the synthesis of these new poly(diazetinediones) with a well-defined structure was achieved for the first time. These polymers were paleyellow, opaque, hard solids with high crystallinity and were insoluble in any solvents. The depolymerization of the polymers occurred drastically at temperatures around 270 °C in nitrogen.

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